THE POTENTIAL CAPACITY OF CARBON FLY ASH COATED WITH POLYELECTROLYTES IN REMOVING CADMIUM FROM WATER

BY

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Dedication

This research work is dedicated to my parents, friends and well-wishers.

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Alhamdulillah, words alone cannot express how grateful I am for everything.

This research work would not have been possible without an amiable, supportive and ever-present professor, am highly grateful to Dr. Bassam Tawabini who stands as my supervisor and advisor. I really appreciate his kind gestures towards the success of this work. He's a rare gem and blessing to me. My sincere and heartfelt appreciations goes to my vibrant, compassionate and ever active committee members; Dr. Tahar Laoui and Dr. Mazen Khaled for their words of encouragement, cautions and constructive criticism. I am highly grateful for your impact in this work.

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LIST OF ABBREVIATIONS

PEFA	:	Polyelectrolyte coated fly ash
RFA	:	Raw fly ash
AFA	:	Acid treated fly ash
PDADMAC	:	Poly (diallyldimethylammonium chloride)
PSS	:	Poly (sodium 4-styrenesulfonate)
FESEM	:	Field-Emission Scanning Electron Microscope
XRD	:	X-ray Diffractometer
EDX	:	Energy Dispersive X-ray Spectroscopy
TGA	:	Thermogravimetric Analysis
FTIR	:	Fourier Transform Infer-Red Spectroscopy
USEPA	:	United States Environmental Protection Agency
ICPOES	:	Inductively Coupled Plasma Optical Emission Spectroscopy
LBL	:	Layer by Layer

ABSTRACT

Full Name : [Olabemiwo Fatai Abidemi]

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Fly ash (FA) is an industrial waste generated from power stations and incineration, its can pollute the environment and adds extra cost for proper disposal. Recent research efforts have consequently focused on developing ways to utilize FA in environmentally-friendly applications such as removing water pollutants by adsorption mechanism methods. In this study, the surface of FA was modified with cationic poly diallyl dimethyl ammonium chloride (PDADMAC) and anionic polystyrene sulfonate (PSS) solutions to produce polyelectrolyte (PE) layers (5 and 20 layers were used) to enhance its capacity to remove cadmium, Cd (II), from polluted water. Surface morphology and chemical composition of the polyelectrolyte-coated fly ash adsorbent (PEFA) was characterized using Field-Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-ray spectroscopy (EDX), Fourier-Transform Infrared (FTIR), X-ray Diffractometer (XRD) and Thermogravimetric analytical (TGA) techniques. Batch mode adsorption studies were conducted to assess the effect of pH, adsorbent dosage, time of contact, initial contaminant concentration, mixing rate and adsorbent layers on the removal efficiency of Cd. The sorption of Cd (II) ions by raw fly ash (RFA), acid treated fly ash (AFA) and $(PEFA)_5$ and $(PEFA)_{20}$ were established to be pH dependent with optimum adsorption achieved at pH 9 yielding 98.6 % removal. The optimum set of parameters for the removal were 4 g/L dose

of adsorbents, 15 min contact time, 150 rpm mixing rate, 2 mg/L of Cd (II) initial concentration and 5 layers PE coated FA. Sorption data at equilibrium were evaluated by Langmuir, Freundlich, and Scatchard plot isotherm models. Their respective R^2 values were well fitted to the sorption data. The dimensionless (R_L) and Freundlich constant (n) indicated a favorable sorption process between the adsorbents and Cd (II) ions in aqueous solution. The results obtained for Scatchard plot analysis indicated the presence of multiple binding sites on PEFA surface which confirmed the good fit in the Freundlich model. The desorption experiment indicated 55% and 35% desorption of Cd (II) ions from the 5 and 20 layers PE coated FA.

ملخص الرسالة

الاسم الكامل : أولابيميو فاتاي أبيديمي

عنوان الرسالة : القدرة المحتملة للرماد الكربوني المتطاير المغلفة بالبولي الكتروليت في إزالة

المجال التخصص الرئيسي : العلوم البيئي

تاريخ الشهادة : ابريل 2017

الرماد المتطاير هو أحد النفايات الصناعية التي تُنتج في محطات توليد الطاقة والحرق، ويمكن أن تلوث البيئة وتضيف تكلفة إضافية للتخلص السليم منها. وقد ركزت الجهود البحثية الأخيرة على تطوير طرق لاستخدام الرماد المتطاير في تطبيقات صديقة للبيئة مثل إزالة ملوثات المياه بطرق مثل آلية الامتزاز. في هذه الدراسة، تم تعديل سطح الرماد المتطاير باستخدام بولي كلوريد الأمونيوم ثنائي الميثيل ثنائي ومحلول سلفونيت البوليسترين الأيونية لإنتاج طبقات بولي الكتروليت واستخدمت (5 طبقات و 20 طبقة) لتعزيز قدرتها على إزالة الكادميوم ، من المياه الملوثة. وقد تم دراسة خصائص التشكل السطحي والتركيب الكيميائي للرماد المتطاير المغلف بالكوليتيروليت باستخدام المجهر الإلكتروني في مجال الأشعة السينية ، الأشعة تحت الحمراء ، والتقنيات الحرارية التحليلية. أجريت دراسات الامتزاز لتقييم تأثير الرقم الهيدروجيني، وتركيز مادة الامتصاص، ووقت المعالجة، وتركيز الملوث، ومعدل الخلط والطبقات الممتزة على كفاءة إزالة الكادميوم. وتم تحديد امتصاص الكادميوم بواسطة خام الرماد المتطاير والرماد المتطاير المعالج بالحمض والرماد المتطاير المغلف بخمس طبقات وعشرين طبقة من البولي الكتروليت لتشكل ايونات معتمدة على الرقم الهيدروجيني، وبأمثل كفاءة امتزاز عند الرقم الهيدروجيني 9 أنتجت كفاءة إزالة تقدر ب 98.6٪. وكانت المجموعة الأمثل من العوامل للإزالة هي أربعة جرامات/ لتر كجرعة من الممتزات، و 15 دقيقة كوقت معالجة، 150 دورة في الدقيقة بالنسبة لمعدل الخلط ، 2 ملغ / لتر من التركيز الأولي للكادميوم ورماد متطاير مغلف بخمس طبقات من البولي الكتروليت. تم تقييم بيانات الامتصاص في التوازن من قبل مخططات نماذج لانجموير، فريوندليتش، و سكاتشارد المتناظرة. قيم معاملات التحديد الخاصة بها توافقت بشكل جيد مع بيانات الامتصاص. الثابت اللابعدي، وثابت و فريوندليتش أظهر أن هناك عملية امتصاص مؤاتية بين أيونات الكادميوم (2) و الممتزات في محلول مائي. وأشارت النتائج التي تم الحصول عليها لتحليل

مخطط سكاتشارد وجود مواقع ملزمة متعددة على سطح والرماد المتطاير المغلف بالبولي الكتروليت الذي أكدت التوافق الجيد في نموذج فريوندليتش. وأشارت تجربة الامتزاز الى نسبة امتزاز 55% و 35% من أيونات الكادميوم (2) بواسطة الرماد المتطاير المغلف بخمس طبقات وعشرين طبقة من البولي الكتروليت.

CHAPTER 1

INTRODUCTION

1.1 Background

The Kingdom of Saudi Arabia faces water challenges because of the presence of arid climatic characterised with an average annual rainfall of 100mm and having groundwater as the major source of water supply for various purposes (domestic, agricultural, industrial etc.). Water is an extremely valuable resource and given the country's rapid population growth, the demand on the limited available water sources is increasing. The excessive extraction of this groundwater source could lead to depletion of water resources in the Kingdom. Low, unpredictable and highly asymmetric rainfall which can be very intensive during local storms. Generally, the rate of precipitation is lower than that of evapotranspiration, with evapotranspiration driven principally by high temperature and dry wind (Abdullah & Al-Mazroui, 2000). The aridity of this region is a result of climatic influences which include the general circulation of the air, distance from a moisture source and local factors such as mountain barriers. Since the water resources is a major factor for domestic, industrial and agricultural activities, the rational development of this resource should be considered as one of the highest priorities in areas with arid conditions like Saudi Arabia (Mahmoud & Sen, 1993). Given the peculiar water demand situation of Saudi Arabia, the need to protect the limited available water sources cannot be overemphasised.

Pollution of water has come to be a life-threatening subject worldwide. Water resources quality is depreciating daily as a result of an increase in industrialisation, changes in environments and geological structures, urbanisation, population increase and activities of agricultural systems (Chong et al., 2010; Zeng et al., 2011, 2013). The constant discharge of different pollutants such as organic compounds and heavy metals into the environment is causing growing concern to the entire world.

Unlike most organic contaminants, heavy metals are mainly problematic because they accumulate in tissues of living organisms and do not biodegrade, thereby leading to countless of threats to the ecological environment and well-being of human at large (Lesmana., et al., 2009). Majorly known heavy metals primarily consist of cadmium, chromium, zinc, mercury, lead, cobalt, nickel, arsenic, copper etc. These metallic ions are toxic and pose severe effects on human well-being. For instance, at high concentration, copper has been regarded to be very lethal globally due to the fact that it's poisoning in humans can lead to health issues like a serious headache, gastritis, nausea, anaemia, loss of hair, damage to the kidney, hypoglycaemia and in worst case scenario, death (Tang., et al., 2012; Rahman and Islam, 2009). In the environment, chromium occurs in form of Cr (III) and Cr (VI). Nevertheless, Cr (III) is less toxic than Cr (VI), of which the toxic effects of Cr (VI) includes gastric and liver damage, skin irritation, lung cancer, as well as kidney problem (Kumar et al., 2007; Selvi et al., 2001).

Cadmium occurs naturally in earth's crust and belongs to group 12 in the periodic table that includes mercury, zinc etc., it is usually found in combined form with other elements like oxygen (cadmium oxide) (ASTRD, 2011). The greatest source of cadmium in the environment is municipal waste incineration, fossil fuel burning coal or oil and through

copper, lead and zinc smelter (Rao et al, 2010). In human, severe intake contact to a high dose of cadmium may have an impact on the lungs, like pulmonary and bronchial irritation. A one-time severe contact to high dosage of cadmium can lead to an everlasting lung impairment function. Cadmium is a deadly heavy metal of work-related and environmental worry. It has been recognised as a substance that is teratogenic and carcinogenic to human as it severely impacts major organs like kidney, liver, reproductive organs and lung (Waalkes, 2000; Filipic, 2012). United States Environmental Protection Agency (USEPA) classify Cd as a class B1 carcinogen. Studies in animal have proven that long-term exposure to cadmium inspiration does lead to an escalation in cancer of the lungs (EPA, 2007). The allowable limit for cadmium in drinking water is given to be 3 ppb by the World Health Organization (WHO) and 5 ppb by the USEPA (Water Quality Association, 2013). Industrial processes like smelting, alloy manufacturing, pesticides, mining, fertilisers, refining, cadmium-nickel batteries among other are anthropogenic ways via which cadmium gets to the environment (Li et al., 2003). Therefore, the necessity for the removal of heavy metals has become an essential one.

1.1.1 Physical and Chemical Properties of Cadmium

Table 1.1 indicates the physical and chemical properties of cadmium. Physically, Cd is odourless and silver-white in colour. Due to its soft nature, it can easily be nicked with a fingernail. Has a melting point of 610°F (321°C), the boiling point of 1,410°F (765°C) and density of 8.65 g/cm3 (ASTRD, 2011). Chemically, it tarnishes in air at room temperature to produce cadmium oxide, even though Cd would not react with water but can react with most acid.

Table 1.1. Summary of Physical and Chemical Properties of Cadmium

Property	**Value**
Molecular weight (g/mol.)	112.41
Colour	Silver-white
Odour	Odourless
Boiling point	765ºC
Melting point	321°C
Density	8.65 g/cm^3
Auto Ignition Temperature	250ºC
Water Solubility (mg/L) @ 20ºC	Insoluble
Vapour Pressure	7.5×10^{-3} mmHg at 257 °C
CAS registry number	7440-43-9

Source: (O'Neil et al., 2006; Faroon et al., 2012)

1.1.2 Treatment of Heavy Metals

Practically, there are countless of techniques used in water treatment with the goal to remove toxic metals. These techniques which are in categories include chemical treatments and membrane technology. Common examples of membrane methods are reverse osmosis and ultrafiltration, however other techniques useful in this regard consist of ion exchange resin, membrane separation, precipitation, electro-coagulation, electrodialysis, reverse osmosis and adsorption (Rao et al., 2010; Sunil et al., 2013). Briefly explained below are some of the above-mentioned principles of remediating toxic metals from water.

Electrodialysis and Electrocoagulation

The process whereby electricity is introduced into an aqueous solution in an electrochemical cell most especially using an aluminium (Al) or iron (Fe) anode. This process is called electrocoagulation. It can electrocute microorganisms and remove more than 99% of some toxic metal ions from water. Electrocoagulation has been applied as an efficient method of the removal of cadmium (Butler et al., 2011). The process of electrodialysis uses ion selective membrane. When an electric potential is applied, positive and negative ions move in the direction of their electrodes that is cathode and anode respectively. Positively charged metal ions are removed through electrodialysis as water. Electrodes are arranged alternatively to produce cells of salts with different concentrations. In the process metal hydroxides are produced, this may result in the clogging of the membrane (Ahalya et al., 2005).

Membrane Filtration

This is a technique that is used in particle separation of liquid from a matrix for its purification. Hani and Moussa investigated on heavy metal removal using membrane filtration technology. Both reverse osmosis and nanofiltration application were researched for removal of toxic metals from wastewater. They find out in their study that reverse osmosis was more efficient with removal efficiency of 90% (Qdais & Moussa, 2004). Adil et al, (2000) studied the application of membrane chromatography for heavy metal removal from the aquatic medium. A very high adsorption rate was detected and an equilibrium was attained in the space of 10 minutes.

Ion Exchange

Ion exchange resin is used in this process to remove metal ions which are positively charged. The exchange of ions takes place between the resin and the ions present in water. The electrostatically attached ions in the resin are replaced by unwanted ions in water. Although this method is a conventional one, yet it has certain disadvantages, one of which is high costs (Ahalya et al., 2005).

Precipitation

Precipitation is a process that involves the adding of chemical reagents to toxic metal contaminated solutions, followed by the filtering of the precipitated solids. Metal precipitation can be achieved by adding coagulants like lime, Iron salt, alum and organic polymers. Among all techniques employed for precipitation process, toxic metal hydroxide is the most frequently used because of its simplicity and low cost. This simple process involves increasing the pH of the contaminated water by using NaOH or CaO for precipitation and therefore immobilise the metals in form of their corresponding hydroxides (Lakherwal, 2014; Rao et al., 2010).

Reverse Osmosis

This technique employs the concept of membranes that are semi-permeable to remove heavy metals from waste waters. The phenomenon behind this method is the pressure created by the dissolved particles in water which is higher in value than the osmotic pressure. Resultantly, the dissolved solids in water are separated from the water content. Reverse osmosis membranes are made up of special polymeric materials which are highly expensive, thereby rendering the technique an expensive one in water treatment technologies (Ahalya et al., 2005).

1.1.3 Adsorption

Adsorption is the process of removing target species from aqueous solution by materials know as adsorbents. Examples of notable adsorbents in activated carbon (AC), synthesised natural sorbents, Nano-sorbents (CNT & CNF) etc. (Pan et al., 2008). The process of sorption has numerous merit such as ease of manufacture, low cost, flexibility, utilisation of domestic and biological waste as adsorbents as compared to other processes, regeneration and reuse-ability, eco-friendly etc.

Adsorption Mechanism

Adsorption mechanism involves the extraction of matter from the solvent phase to a concentrated phase known as the sorbate. This surface phenomenon is a result of surface energy. All the required bonds in a bulk matrix (covalent, metallic or ionic) of the component atoms are filled by other atoms in the material. Nevertheless, atoms on the sorbent surface are not partially encircled by atoms of other sorbent and thus can attract sorbates. The bonding nature often depends on the contents of species in question. The sorption process can be categorized as physical adsorption characterized by weak van der

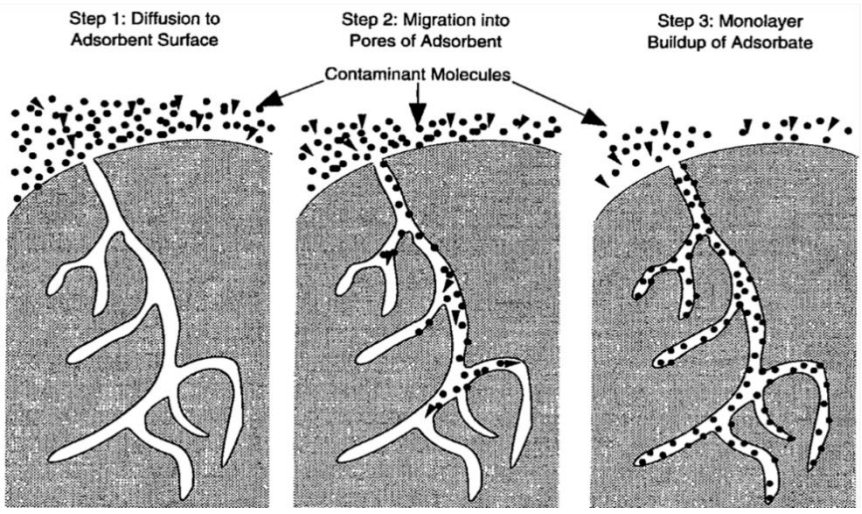

Figure 1.1 Annotation of the mechanism of adsorption

waals forces or chemical adsorption characterized with covalent bonding or exchange adsorption which is due to electrostatically charge sites (Ferrari et al., 2010). Adsorption mechanism is demonstrated in Figure 1.1 above.

1.1.4 Using FA for Heavy Metal Removal

A key contemplation of choice for any remediation technology is cost, hence the use of FA for the removal of toxic metals has the prospect in fulfilling these key requirements. FA is narrowly similar to volcanic ashes used in making of the primitive identified hydraulic cements about 2,300 years ago. Millions tonnes of FA are produce yearly by local industry to make it readily available. FA is one adsorbent that can be acquired with little or no cost and it has an excellent adsorption capacity for heavy metals removal. Adsorption capacity of 1.39 mg/g, 2.92 mg/g and 2.82 mg/g was recorded for Cu (II), Cr (VI) and Hg (II) in a study conducted for the removal of these metal ions in waste water (Wang et al., 2016). Acid treatment is one way by which the sorption capability of FA can be enhanced, and it is briefly explained in the next paragraph.

Acid Treatment

Acid treatment is the addition of a functional groups to the surface of a material through chemical synthesis techniques, it is also known as Functionalization. This can also be regarded as modification of material (CNT, CNF, FA etc.) surfaces for attainment of preferred surface characters such as water repellent coatings (Fu & Wang, 2011). Furthermore, functional groups (esters, carbonyl, hydroxyl etc.) had been mostly used to link molecules covalently to biochemical and chemical equipments such as micro-electromechanical and microarrays systems (Muthukumaran & Beulah, 2011). Organic or inorganic polymers can be attached to a material that has been functionalized. For example,

FA was functionalized with HNO_3, H_2SO_4, or HCl of which the product contains an –OH or a COO^- functional groups (El-sherif & Fathy, 2013). Functional groups are covalently links to wide array of particles like nanoparticles and other composites of interest to be applied in various fields like water treatment research and so on.

Impregnation

Impregnation is one technique that is frequently used to produce heterogeneous materials such as AC, FA, CNT, CNF etc. It is also known as incipient wetness or decoration. This technique requires bond creations and scissions. it takes place more often during thermal initiation of the drying process. The interaction strength of the impregnation technique is the role of the bond between the metal ions and the material surfaces which can easily be reversed (de Jong, 2009). Generally, metal precursors are dissolved in an organic or aqueous solution. Concurrently, a solution containing the metal of interest is added to a material with similar pore volume as the solution volume. The solutions enter the pores through the means of capillary action. There can be changes the process by which the solution get into the pores from the process of capillary action to diffusion process if the solution volume is greater than the pore volume. Drying and calcination of the material can then take place to remove the volatile components in the solution, thereby depositing the metal on the material surface. The level of concentration of the impregnated component depends on the conditions of mass transfer inside the pores during drying and impregnation (Copéret, 2010).

1.1.5 Polyelectrolytes

Polyelectrolytes are organic polymers which are soluble in water and are formed from monomers of different kinds. Polyelectrolytes improved the efficiency of a wide-range of

vital processes. They convey ionic charges alongside chains of polymers. These polymers could be cationic or anionic depending on the charge but some bears both cationic and anionic groups called polyampholytes (Bolto & Gregory, 2007). Their unique properties ensure they can be seen in a numerous number of applications: for water purification, wastewater treatments, paper production, and as a thickening agent in health care products comprising shampoos, soap, and body lotions. Polyelectrolytes are also used as additives to modify the physical properties of aqueous solutions. Some examples are adhesive strength, film formation, and protective colloidal and suspending actions (Pyun et al, 2003). More recent applications that use polyelectrolytes are drug and genetic material delivery vehicles. One of the main advantages of polyelectrolytes, also due to their macromolecular properties, is the fact that their use is not limited to solution or aqueous form alone. Polyelectrolytes can also be processed to become surface coatings, which is highly desirable for interfacial and surface processes.

Figure 1.2 gives some examples of polyelectrolytes with their structures: poly diallyldimethylammonium (PDADMAC), poly styrene sulfonate (PSS), poly ethylenemine (PEI), poly (ether ether ketone) (SPEEK), poly (N-octadecyl-2-etheynyl-pyridinium bromide) (PNO_2EPB) etc.

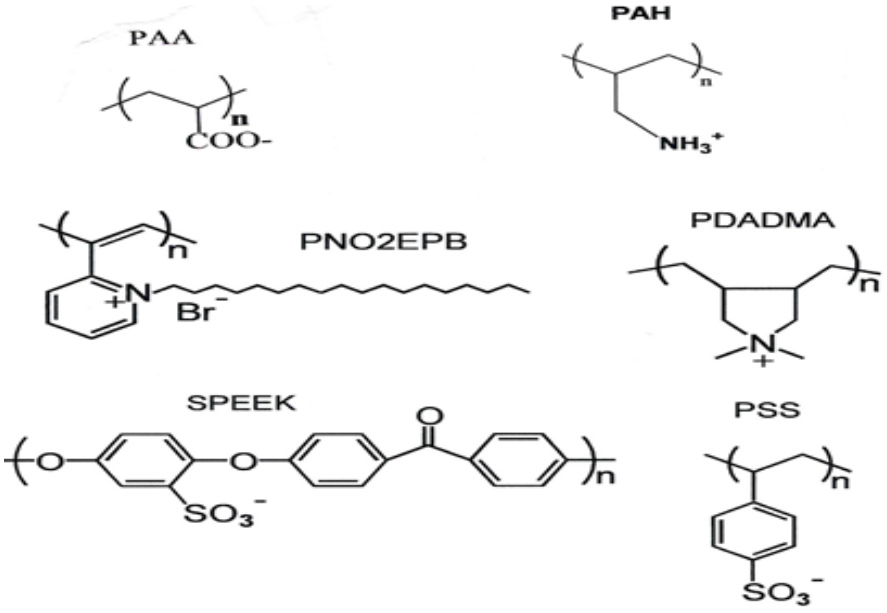

Figure 1.2 Structures of some polyelectrolytes (Bolto & Gregory, 2007)

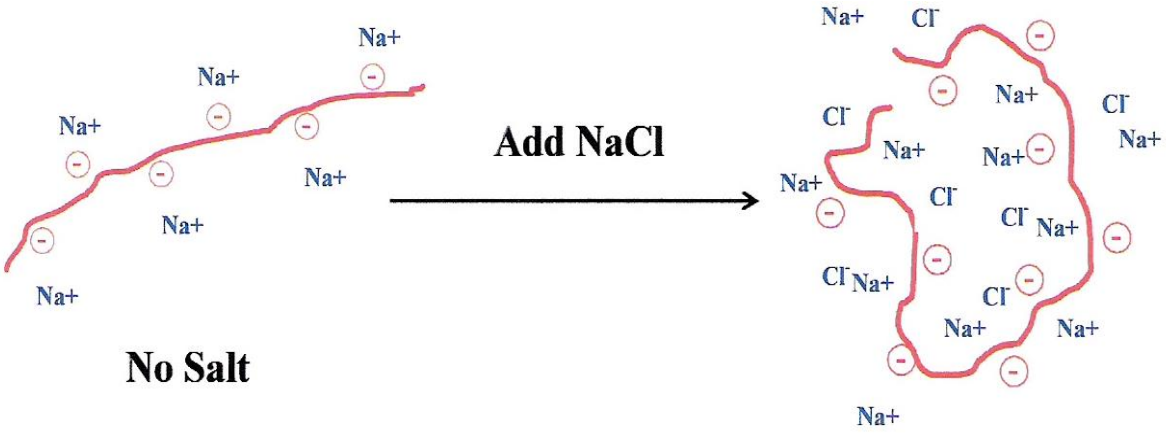

Figure 1.3 Schematic illustration of ionic strength influence of polyelectrolyte molecule shapes in solution (Wang, 2009)

The strenght of solutions in which polyelectrolyte is prepared can be very essential. A polyelectrolyte, in low ionic strength solutions, tends to be in its most extended and uncoiled form due to the intermolecular repulsion of the unscreened charges on each monomeric unit of the macromolecule. On the other hand, when the ionic strength of the solution is increased, a polyelectrolyte tends to become more coiled due to the screening effects of polymer charges by the excessive presence of smaller salt counterions in solution, as shown in Figure 1.3.

1.1.6 Layer by Layer Self-Assembly Technique

The layer-by-layer (LBL) assembly technique was first mentioned by Iler in 1966. Nevertheless, in 1991 Decher and Hong extended that practice and brought it to the pole position of materials science and engineering (Bolto & Gregory, 2007). Since then, research in this field has attracted the attention of scientists across the academic and industrial fields. In April 2005, about 1600 publications utilizing this technique were reported. Figure 1.4 shows an annotation of a detailed layer-by-layer assembly process. Therefore, one can build as many layers as desired depending on the task such experiment lingers on. One advantage of the LBL technique is that it is reproducible, robust, environmentally and cost friendly method. The technique is mostly conducted at room temperature, therefore special instrumentation or vacuum equipment are not required. It can be used to assemble various types of materials, polymers, composites, clay, proteins, dyes, carbon nanotubes or nanoparticles (Pyun et al, 2003).

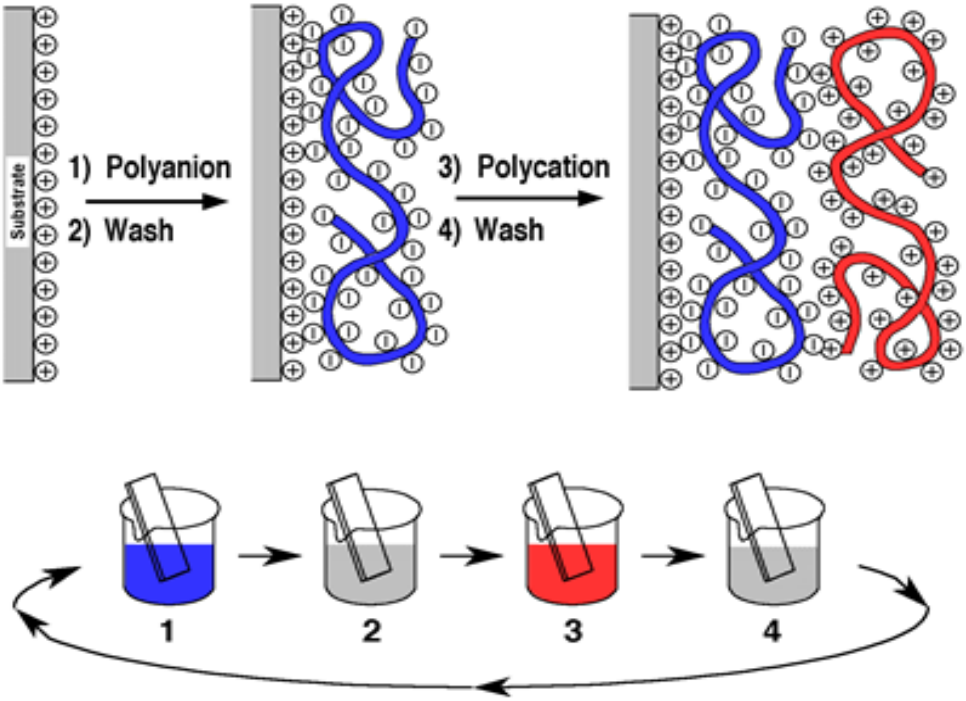

Figure 1.4 Schematic illustration of LBL deposition techniques (Pyun et al, 2003)

1.2 Statement of the Problem

Toxic metals are very dangerous pollutants of water which adversely affect the health of human, leading to disease that are often fatal. Due to this above-mentioned fact, water treatment has become very essential in the present day. Population growth, technology advancement, urbanization among others are specifically at a geometric scale which in turn can lead to activities that release contaminant to the environment. Water is a very important component of our life as human and over 90% of our body composition is water. Therefore, clean and purified water is needed for consumption. Most toxic metals are sparingly soluble and swiftly dissolves in groundwater, migrating farther and faster due to industrial, municipal or agricultural activities. To remove pollutant in water, several remediation

technologies such as adsorption with activated carbon or nano-materials like carbon nanotube, air stripping, phytoremediation, ultraviolet/hydrogen peroxide treatment have recorded varying levels of success and each technique is characterized by its inherent limitations, which create the opportunity for further research into the removal of toxic metals from contaminated water.

1.3 Significance of the Study

Sustainable development in Saudi Arabia entails maintenance of the limited water sources available. As it is commonly known that toxic metals are very perilous water contaminants due to their adverse impact on the health of human. Even though one may not see the negativity of these contaminants at once, chronic exposure can lead to declining health as mentioned above. Though enquiries indicated that it is imperative to get rid of these heavy metals to safeguard human health, for this purpose treatment of water is necessary. There are several water treatment techniques being incorporated with numerous sets of materials in their treatment. One drive in this research is to improve water quality. As noted from literature, fly ash (FA) has been applied in the treatment of water severally. In addition, one candid drive towards conducting this study is modifying the existing approaches which are being used by coating FA with cationic and anionic polyelectrolytes (PDADMAC & PSS) respectively. As it is widely known that numerous studies have been carried out on the use of FA as an adsorbent in water treatment but little is known on the layer by layer deposition of polyelectrolyte solutions on FA in removing cadmium. This gap that has left unfilled need to be occupied and the successful trial of new substances is still a challenge which must be embark on in this particular circumstance.

This study focuses on the use of FA coated with polyelectrolytes. FA is a waste product from a local industrial power plant that can be employed in the removal of toxic metals in contaminated water sources. The utilization of a local industrial waste serves as a form of waste reuse which is sustainable, therefore enhancing the waste management process of the Kingdom. Also, this experimental outcome make available a cost effective and more productive alternative in the removal of toxic metals from contaminated water sources and further support plans to provide portable water supply to citizens and residents in the Kingdom as well as increase scientific knowledge on removal of toxic metals in water sources.

1.4 Research Objectives

The main objective of this research was to evaluate the efficiency of polyelectrolytes coated FA in the removal of cadmium (Cd) from contaminated water.

The specific objectives are:

1. To prepare and characterize raw FA (RFA), acid treated FA and polyelectrolytes coated FA (PDADMAC-PSS FA).
2. To demonstrate removal of Cd from contaminated water using polyelectrolytes coated FA under bench-scale condition.
3. To study the effect of solution conditions such as pH, contact time, dosage, mixing rate, initial concentration of metal ion, and temperature on the adsorption efficiency.
4. To evaluate the adsorption isotherms and kinetics under the optimum treatment conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Cadmium Removal

Numerous studies on Cd (II) removal has been carried out using various techniques (Kulkarni & Kaware, 2013). Mahvi & Bazrafshan, 2007 applied electrocoagulation for cadmium electrode, artificial wastewater of different concentrations of Cd (II) were filled in a tank and their removal were measured at different pH (3, 7 and 10) and at 20, 30 and 40 volts' electric potential range. Their investigation showed that initial pH was lower than the final pH value. In 2000, Wang and his research group study the Cd (II) precipitation on cell surfaces by sulphur reducing aerobic bacteria (Wang et al., 2000). Sulphide secretion was made possible through an aerobic reduction pathway. This pathway cultivates a certain bacterium that aids the precipitation of Cd (II) into cadmium sulphide. Wang research group concluded that the process cannot be immediately incorporated into toxic metals removal and that more work still needs to be done (Wang et al., 2000). In 2011, Zhang, et al, (2011) extracted from an aqueous medium a pre-treated biomass needed for the removal of Cd (II). During their study, they observed that maximum efficiency for removal of biomass was at pH 5 which occurred in the initial 35 minute of the reaction.

Ion floatation technique has been used by Walkowiak and Małgorzata in the separation of Cd (II) and Zn (II) from a solution of sulphate. They study on the separation of Cd (II) and Zn (II) ions from aqueous medium of sulphate which contains equal molar mixture on both

metal ions through ion flotation and transport via processes of polymer inclusion membrane (Malgorzata et al., 2003). In 2004, Bell and Saunders investigated polyelectrolytes effect on Cd (II) adsorption with aluminum oxide. They found out that adding millimolar polyelectrolyte concentrations increased Cd (II) ions removal from a 29.7 micrometer aqueous medium via aluminum flocs from 40 to 70 % (Bell & Saunders, 2005). Also, Srivastava et al., (1998) used mixed oxides of aluminum and iron to investigate Cd (II) adsorption behaviour.

One of the most encouraging method which is applicable in heavy metals removal is adsorption. In 2013, Al-Khadi and his research team investigated the efficiency of four kinds of adsorbent which consist of carbon nanotube (CNT), activated carbon (AC), carbon nanofiber (CNF) and fly ash (FA). They observed that at contact time of 120 minutes, PH 7, and mixing rate of 150 rpm raw fly ash remediate 95 % cadmium from water while CNT, CNF and AC removed 27 %, 34 % and 38 % Cd (II) respectively. The adsorbent experimental data fit well with Langmuir and Freundlich adsorption model (Al-Khaldi et al, 2013). Mihaela et al., 2002 used low adsorbent materials like activated carbon, diatomite, and bentonite. Bentonite was found to be very efficient which shows 99 % Cd (II) ions removal in the presence of copper as compared to others. The adsorption process equilibrium tailored Langmuir and Freundlich isotherms for all the adsorbents. Maleki et al, (2011) research on Cd (II) ions adsorption using barley hull ash and barley hull as adsorbent. It was observed that increase in efficiency removal correlate with varied pH. Their study indicated maximum adsorption was around 99.2 % and 95.8 % for barley hull ash and barley hull respectively. Contact time, optimum pH and initial concentration were detected at 180 minutes, pH 9 and 30 ppm concentrations respectively (Maleki et al., 2011).

Boparai and its research team study Cd (II) ions adsorption on nano zerovalent iron particles. They as well studied its kinetic and thermodynamic processes. The research was accompanied at 25-480 ppm concentration range. It was detected that adsorption increases as temperature and endothermic reaction increases (Boparai et al., 2011). They observed that the process of adsorption fit well into the Temkin and Freundlich isotherm model and was a second order. Goran and his research group removed Cd (II) from aqueous solutions using chemically oxidized multiwalled carbon nanotube (MWCNT) and MWCNT functionalized with ethylenediamine. It was observed that ethylenediamine functionalized MWCNT was more efficient in removing Cd (II) from the aqueous solution (Goran et al., 2010).

2.2 Fly Ash Utilization

Adebayo and his research teams investigated the efficiency of raw fly ash and silver oxide impregnated fly ash for the removal of MTBE (methyl tertiary butyl ether). It was observed that silver oxide impregnated fly ash was able to remove 24 % MTBE from aqueous solution (Adebayo et al, 2016). Nollet et al, (2003) used fly ash to remediate polychlorinated biphenyls (PCBs) from wastewater at dosage of 5 g/L, pH 7 and 25 ^{0}C. The fly ash was able to remove 97 % of the PCBs. Maria et al investigated the removal of cadmium using modified fly ash (Maria et al., 2008). The adsorbent used was modified with complexion agent and alkaline medium for lengthy period. During experimentation they observed that sodium hydroxide concentration in optimized conditions is enough for creating a substrate and can bring about 97 % Ni (II) and Cd (II) ions removal in a great range of concentration (Maria et al., 2008).

Mohan et al., (2009) reported the prospect of exploiting coal fly ash for heavy metal ions adsorption [Pb (II), Zn (II), Mn (II), Cu (II) and Cd (II)]. In order to find the kinetic features of process of adsorption, data of the experiment were assessed. Langmuir and Freundlich isotherms model was used to describe the isothermal data of the adsorption. Concentration of fly ash that was needed to reach maximum removal of heavy metals was detected to be 2 g/L with removal efficiencies of 28 %, 39 %, 42 %, 71 % and 74 % for Mn (II), Cu (II), Zn (II), Cd (II) and Pb (II) correspondingly. Results of the investigation established that fly ash can be used as an efficient low cost adsorbent for heavy metal ions. Pb (II), Zn (II), Mn (II), Cu (II), Cd (II)and Ni (II) removal from polluted liquids has been researched on several kinds of fly ashes (Chaiyasith et al., 2006; Koukouzas et al., 2010). The outcomes of various investigation propose that fly ash may well be an encouraging adsorbent on condition that environmental technologies improved in years yet to come.

2.3 Polyelectrolyte-Coated Adsorbents Utilization

Zhang et al, (2011) conducted an experiment on Cr (VI) removal by using multi-walled CNT wrapped with cationic polyelectrolyte (PDDA). The modified adsorbent was able to remove 32 % attained at pH 6. Huang and his group of investigators successfully applied Silica-coated Fe_3O_4 functionalized with c-mercaptopropyltrimethoxysilane for extraction of Cu (II), Hg (II), Cd (II), and Pb (II) in a varied pH range and even in the presence of foreign ions acting as interferents such as Al (III), Fe (III), and Cl^- (Huang et al., 2008).

Yang et al, (2009) arranged a redeveloped photocatalyst of cadmium sulfide (CdS) via CdS nanoparticle coating incorporated in mesoporous silica spheres (hexagonal shape) with layers of polyelectrolyte. These coated catalyst successfully degenerate some phenolic

compounds and dyes for more than 22 runs short of Cd (II) species leakage into the solution. Muñoz & Aller, (2012) modified coal fly ash using mercaptoethanol to retain small level lead from aqueous solution.

Several studies have identified that using polyelectrolyte such as poly (amidoamine) dendrimers, polyethylene imine hyperbranched polymers, poly (propylene imine) etc. for modification increased sorption efficiency for remediating different kinds of organic pollutants from water (Yates & Hayes, 2004; Savage & Diallo, 2005; Arkas et al, 2007). Khaydarov et al, (2010) produce polyethyleneimine conjugated carbon nanoparticles which were used for remediating toxic metal ions from water. 4.0–5.7 mmol/g capacity was attained for divalent ions, of which the sorption rate of Hg (II), Pb (II), Zn (II), Mn (II), Cu (II), Cd (II)and Ni (II) and Cr (VI) was almost 99 %. Maebana and his research team studied the efficacy of ethylene vinyl acetate-fly ash (EVA-FA) for phenolic compounds remediation (Maebana et al, 2013). At pH 4 and 5 adsorptions of the phenolic compounds was 83 % and 76.3 % respectively. Atieh assess the proficiency of modified and non-modified CNFs for removal of Zinc from water (Atieh, 2011). The study indicated that pure CNFs was not effective but a great removal of about 97 % happens at pH 7 when CNFs functionalized with carboxylic acids group was applied. He attributes the very strong removal to the affinity of Zinc to the physical and chemical properties of the functionalized CNFs. Stanton et al (2003) show that alternating polyelectrolyte deposition on porous supports can yield nanofiltration membranes that allow high water flux along with selective ion transport by using pairs of poly (styrene sulfonate)/poly (allylamine hydrochloride) on porous alumina.

2.4 Research Gap

As gathered from literature, fly ash and other adsorbents had been used for heavy metal removal. In recent time, huge effort had been added to modified previously existing adsorbents efficiency and develop new ones. For instances, alumina was an effective adsorbent for the removal of Cd (II) from water but it comes at a cost which might be expensive to apply in large scale. On the other hand, fly ash is a waste and can easily be collected at little or no cost. From previous studies, it is known that fly ash performance has not been encouraging in toxic metal removal. Nonetheless, non-modified alumina was not significantly efficient in removing cadmium as noted by Bell and Saunders (2005), its performance increased after modification with the polyelectrolyte. The outcomes of various investigations by Bell and Saunders (2005), (Maria et al, 2008) and other researchers on coating a substrate with polyelectrolytes suggest that the removal capacity of heavy metal ions by an adsorbent could be improved by this technique. Hence, in this study the surface charge of FA was enhanced with cationic poly (diallyl dimethyl ammonium chloride): PDADMAC (Mw = 200,000– 350,000) and anionic poly (sodium 4-styrenesulfonate): PSS (Mw = 70,000) respectively through LBL deposition technique to increase FA efficiency in cadmium removal from contaminated water.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals/Stock Solutions

All chemical reagents (HNO_3, NaOH, $Cd(NO_3)_2.6H_2O$ etc.) used were of analytical grade. PDADMAC (Mw: 200,000-350,000 kg/mol.) and PSS (Mw: 70,000 kg/mol.) were used. Deionized water was generated in real-time from Milli-Q ultrapure water system. 2 mg/L of Cd (II) solution was prepared from standard solutions which contain 1000 mg/L concentration of $Cd(NO_3)_2.6H_2O$ was prepared in a 1000 mL volumetric flask with deionized water. The solution was stirred with a magnetic stirrer to ensure the mixture is homogeneous. The pH of the solution was adjusted using either of 0.1M HNO_3 or 0.1M NaOH solution. The addition of the buffer solutions was included to keep constant pH during the experiment.

3.2 Adsorbent Preparation

The raw fly ash used in this study was obtained from a local power plant in the Eastern Province of Saudi Arabia. In this plant, raw fly ash is generated from the combustion of heavy liquid fuel and collected by electrostatic precipitation technique. Three (3) sets of the fly ash materials were used, namely; raw fly ash (RFA), acid-treated fly ash (AFA) and polyelectrolyte coated fly ash (PEFA).

3.2.1 Acid Treatment of Fly Ash

One hundred and fifty (150) g of this fly ash materials was soaked in deionized water in a 1000 mL beaker and stirred for 2 hours. After stirring, the mixture was allowed to settle for 10 minutes, before the water was decanted. The procedure was repeated 3 times and the slurry phase was dried inside the oven at 80^{o}C for 12 hours and stored for the batch treatment experiments. One hundred (100) g of washed fly ash was soaked in 300 mL of 1M HNO_3 (50 mL acid in 800 mL of deionized water). The mixture was refluxed at 105^{o}C for 24 hours. The acid was allowed to evaporate at 60^{o}C, after which the reaction mixture was diluted with 500 mL deionized water until the pH of the filtrate becomes neutral. The residue was then dried in the oven at 105^{o}C for 72 hours as shown in Figure 3.1. The procedure followed by many researchers including (El-sherif & Fathy, 2013; Asmaly et al., 2016; Parvez et al, 2014; Shawabkeh et al, 2011; Shawabkeh, 2006; Abuilaiwi et al, 2010; Li et al, 2011).

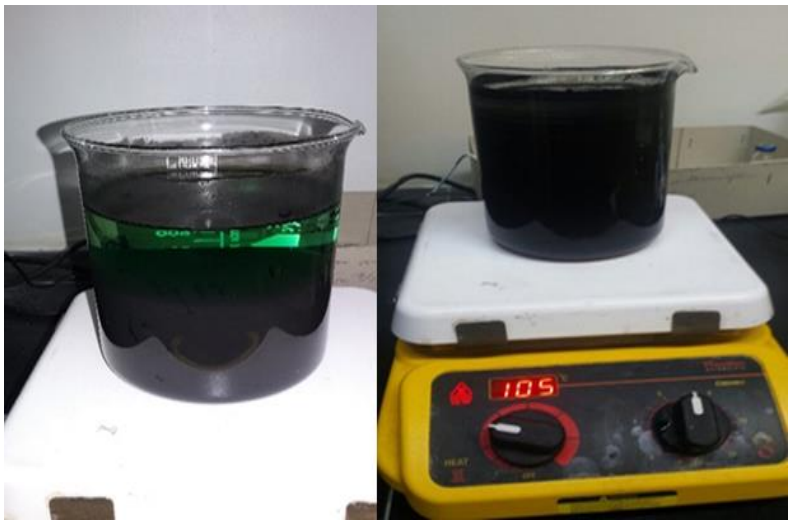

Figure 3.1 Image showing acid treatment of Fly Ash

3.2.2 Layer by Layer (LBL) Deposition of Polyelectrolyte on FA

The procedure involves alternating exposure of a charged substrate to solutions of positive and negative polyelectrolytes, respectively, with rinse step in between to remove any extra material that is loosely bound to the surface. Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilized by strong electrostatic forces. Such self-assembled polyelectrolyte multilayers (PEMs) have proven to be versatile materials with respect to the incorporation of different charged compounds (Li et al, 2011).

In this study, 3 mL of poly diallyl dimethyl ammonium chloride (PDADMAC) was dissolved in 1000 mL of deionized water, the solution was stirred with a stirrer to ensure a homogenous mixture. The procedure was repeated for 3mL/L of polystyrene sulfonate (PSS) solution as shown in Figure 3.2. 40 mL of a PDADMAC solution was poured into a beaker containing 20 g of AFA, this was stirred 10-15 minutes, after which the mixture was allowed to stand until there is a clear separation between the residues and filtrate. The filtrate was filtered out and the residue which remains in the beaker was rinsed with deionized water and stirred for 10-15 minutes. Under the similar conditions, 40 mL PSS solution was added to PDADMAC layered FA to obtain a one layer PDADMAC/PSS-FA as shown in Figure 3.3 and 3.4. The procedure was repeated until the desired number of layers was attained i.e. $(PDADMAC/PSS\text{-}FA)_n$ where n could be 1,2,3,4,5….20 (Li et al., 2011).

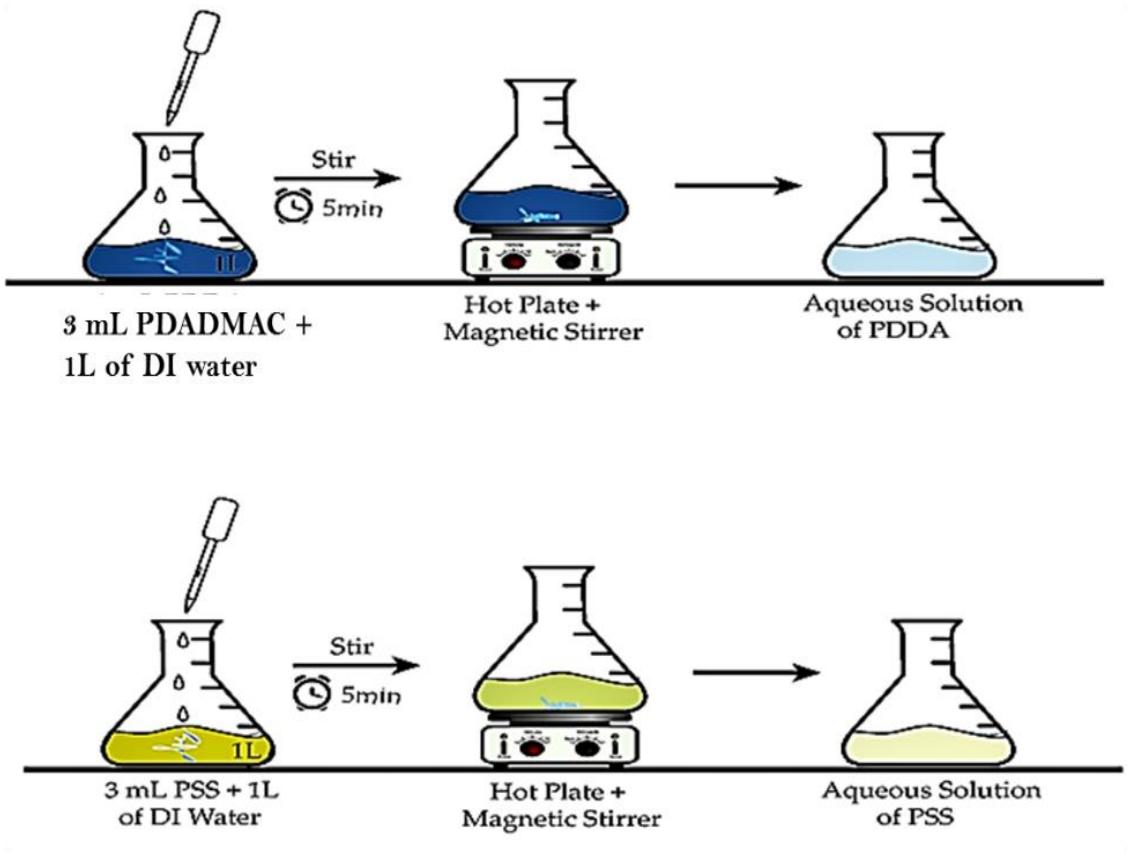

Figure 3.2 Diagrammatic annotation of PDADMAC/PSS aqueous solution preparations

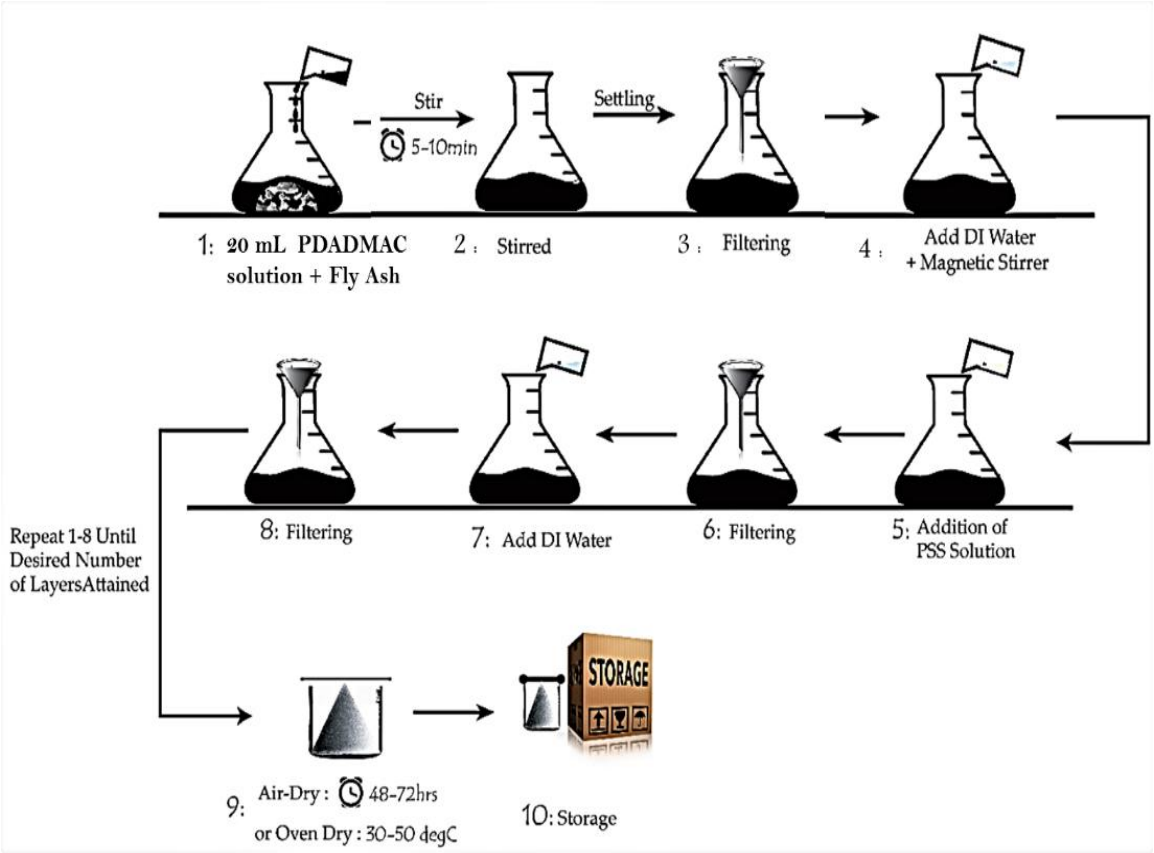

Figure 3.3 Diagrammatic annotation of LBL coating of fly ash with polyelectrolytes

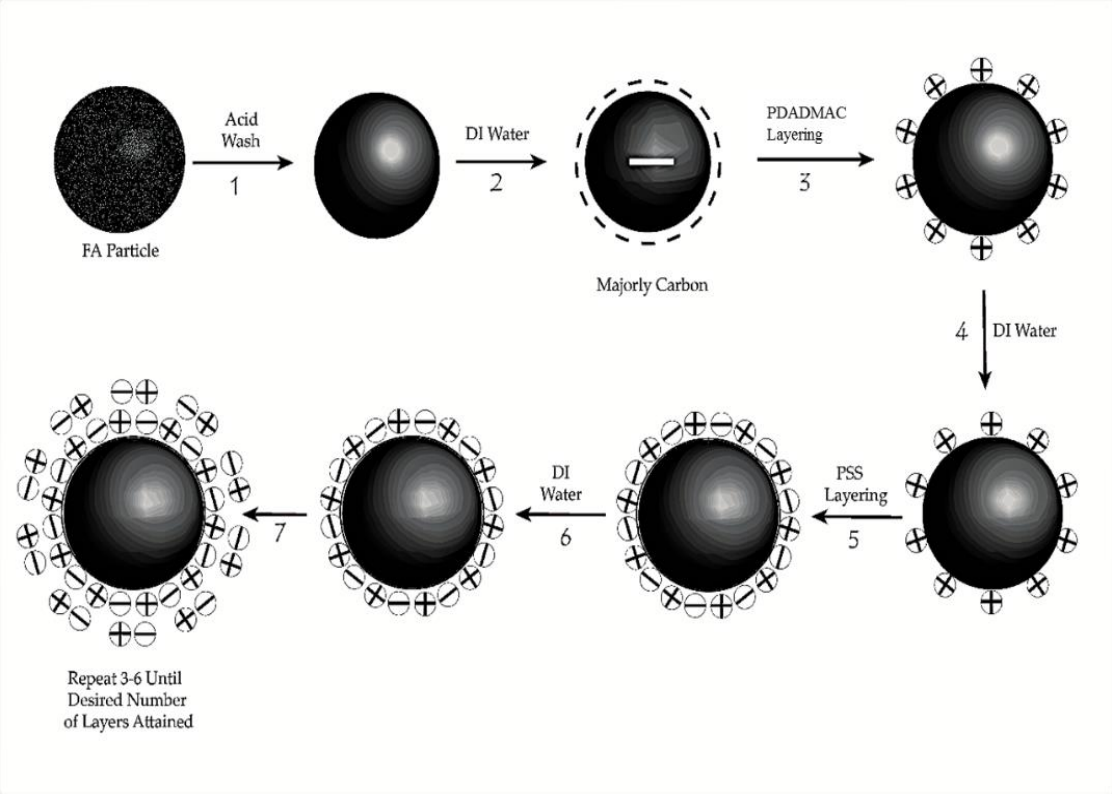

Figure 3.4 Schematic annotation of acid treatment and LBL coating of fly ash with polyelectrolytes

3.3 Material Characterization

Characterization of adsorbents (RFA, AFA & PEFA) surface was conducted to determine the morphology, as well as the elemental, phase and functional group composition of the materials.

3.3.1 Field Emission Scanning Electron Microscopy (FESEM)

To examine the surface morphology of the materials, field-emission scanning electron microscopy (FESEM) (TSCAN Mira 3) was used as shown in Figure 3.5. Thin conductive layer of gold was applied on the surface of the samples. Low voltage back-scattered electron (BSE) and secondary electron (SE) imaging were used to acquire images.

Figure 3.5 Field Emission Scanning Electron Microscopy (FESEM)

3.3.2 Energy Disperse X-ray Spectroscopy Analysis (EDXS)

In order to identify the type of elements on the surface of the adsorbent materials, an EDX detector connected to the FESEM unit was used in this study. Characteristic x-rays could be generated from the sample if exposed to electrons of minimum kinetic energy.

3.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using thermal analyzer (Q600 SDT) by TA instrument, USA as shown in Figure 3.6 to evaluate the changes in sample weight due to temperature increase. About 5-10 mg of prepared adsorbent materials was mounted on an aluminum crucible. The analysis was conducted in an inert (N_2) atmosphere at a distinct temperature ramped at 10 ^{0}C per minute to 900 ^{0}C with a flow rate of 20 mL/min.

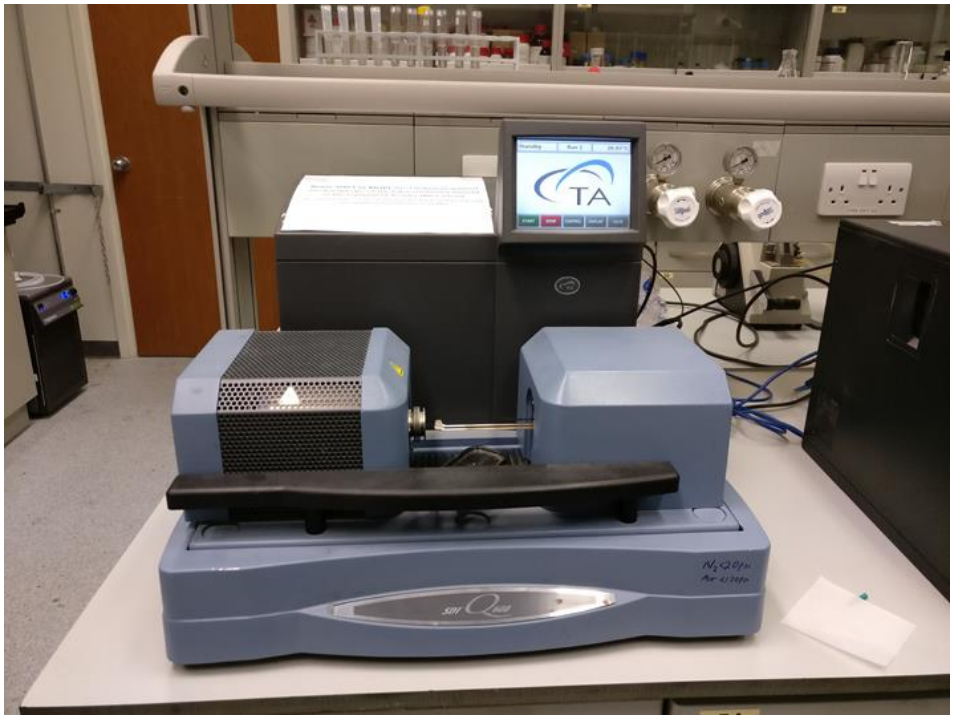

Figure 3.6 Thermogravimetric analysis unit

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR technique was employed to ascertain the functional groups present in both treated and untreated fly ash surface with the aid of TENSOR 27 FTIR spectrometer by BRUKER, Netherland as shown in Figure 3.7. About 1 mg of both treated and untreated fly ash adsorbent materials were carefully placed on the diamond lens using the Attenuated Total Reflectance (ATR). The materials were scanned from 500-4000 cm^{-1} wavenumber and the spectrum of materials was observed.

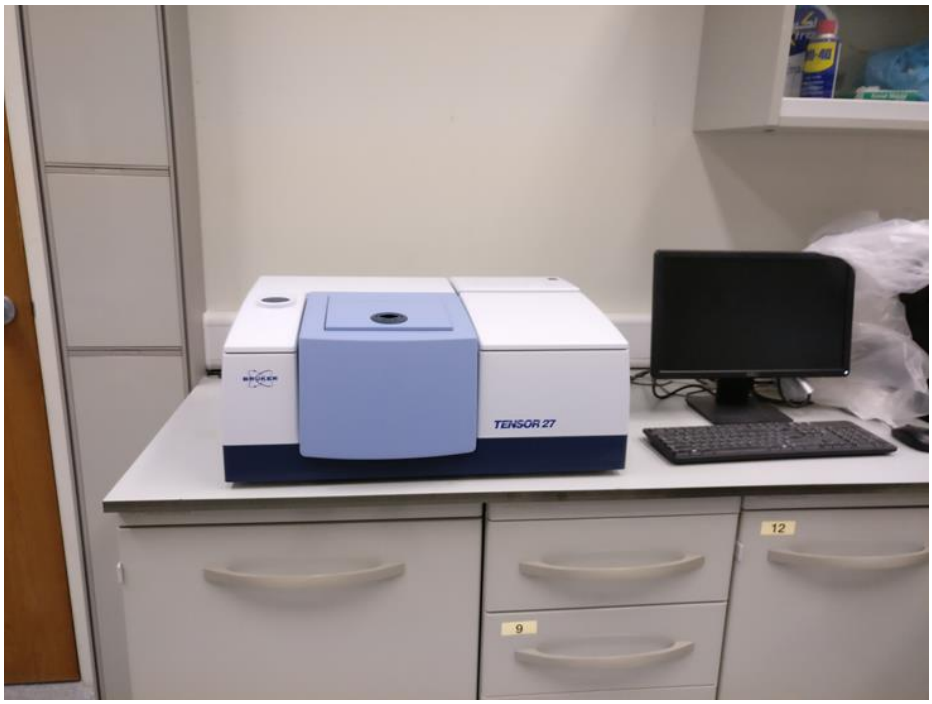

Figure 3.7 Fourier Transform Infrared Spectroscopy (FTIR)

3.3.5 XRD (X-ray Diffraction) Measurement

Phase analysis of the adsorbents was performed on D8-Advance X-ray Diffractometer manufactured by BRUKER (USA) as shown in Figure 3.8. Sample holders were filled with

treated and untreated adsorbent materials (RFA, AFA, and PEFA). The samples were tested at 40 kV and 30 mA, spectra of the samples were obtained at Bragg angles of 10°-100°.

Figure 3.8 D8-Advance X-ray Diffractometer

3.4 Adsorption Studies

Two (2) mg/L Cd (II) solution was added to deionized water and subsequently treated on batch mode using various doses of prepared adsorbent materials (RFA, AFA, and PEFA).

3.4.1 Preparation of Cd (II) Aqueous Solution

All glassware utilized in this study were rinsed with 2-5 % nitric acid to ensure there are no impurities and prevent adsorption of heavy metals to the walls of the glass wares. The stock solution used for this research was prepared from 99.99 % purity (ICP grade) Cd standard solution purchased from ultra-scientific. Deionized water generated from Milli-Q

ultrapure water system was used in diluting the stock solution to preferred concentrations employed in the batch experiment. 2 mL of Cd stock solution was pipetted into 1 L volumetric flask and mixed thoroughly. Equation (3.1) given below was used to determine the volume of Cd (II) that would be required for the dilution.

$$V_1C_1 = V_2C_2 \qquad (3.1)$$

Where V_1 is volume of standard solution (L); V_2 is required volume of deionized water for dilution (1L); $C_1$is the concentration of standard solution (1000 mg/L) and C_2 is the concentration of stock solution to be prepared (2 mg/L). The pH of the aqueous solution was then adjusted with either of 1M HCl or 1M NaOH to the needed pH.

3.4.2 Batch Mode Adsorption Studies

Batch mode adsorption studies were examined at room temperature in 100 mL Erlenmeyer flasks covered with aluminum foil to avoid contamination. Erlenmeyer flasks containing 50 mL of Cd ion solutions were mounted on an orbi-shaker (Figure 3.9) at 298 K temperature, while altering the experimental parameters which includes the dose of adsorbents (1-6 g/L), mixing rate (50-250 rpm), contact time (5-120 min), initial pH of aqueous solution (4-10), initial concentration of Cd (II) ions (1000-10,000 µg/L), and adsorbent type (RFA, AFA, and PEFA). After mixing for the required period of time, the suspension was filtered through 0.45 µm Millipore filter papers. About 3 mL of the samples were collected and analyzed using the ICP/ OES (Inductively Coupled Plasma Optical Emission Spectrometry) manufactured by Perkin-Elmer as shown in Figure 3.10. For each of the effect studied, control experiment was conducted to determine precipitation effect.

Duplicate samples were collected and analyzed as a form of quality control measure to ensure experimental results accuracy.

The amount of Cd (II) ion adsorbed onto the surface of adsorbents materials (RFA, AFA, and PEFA) were calculated by equation 3.2 & 3.3 (percent removal and adsorption capacity of metal ions).

$$\% \text{ removal} = \frac{C_i - C_e}{C_i} \times 100 \qquad (3.2)$$

$$\text{Adsorption capacity}, q_e(\text{mg/g}) = \frac{C_i - C_e}{M_s} \times V \qquad (3.3)$$

Where C_i is the metal ion initial concentration in solution (mg/L), C_e is the final concentration of adsorbate ion in solution (mg/L), V is the total volume of solution (L), M_s is Adsorbent dosage.

Figure 3.9 Orbi-shaker used for batch experiment

Mean values of 3 replicates were used for data analysis to ensure reproducibility, relative standard deviation (RSD) ranges from ± 3-5 %. The precision of the standard solution for analysis was better than 3 %.

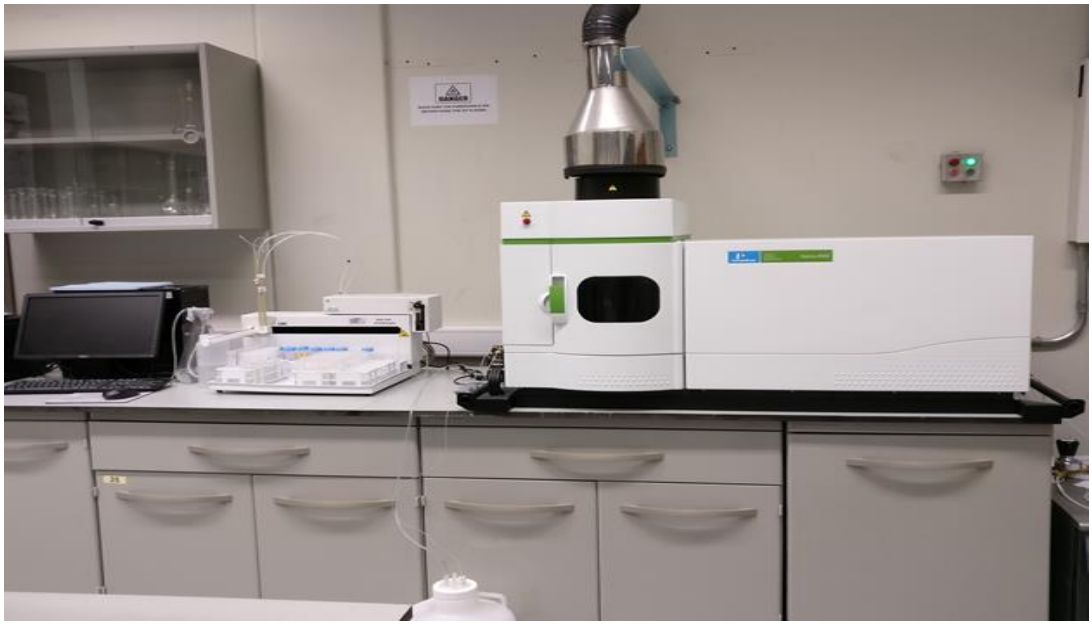

Figure 3.10 Inductively Coupled Plasma Optical Emission Spectrometer (ICP/ OES)

3.4.3 Desorption Study

Desorption experiment was conducted by stirring 4 g/L of the adsorbents ($PEFA_5$ and $PEFA_{20}$) in 50 mL Cd (II) ion solutions for 60 minutes. The loaded adsorbents were then filtered, dried to constant weight and subsequently dissolved in 50 mL 0.1 M nitric acid after which the mixture was mounted on an orbi-shaker and agitated for 24 hrs. The suspension was filtered with 0.45 µm millipore filter paper and 2-3 mL of the filtered solution was analyzed with ICP/ OES to determine the quantity of Cd (II) ions desorbed in the filtrate. The percent desorption of Cd (II) ions was calculated by equation 3.4 below:

$$\% \text{ Desorption} = \frac{C_d V_d}{q_e W} \times 100 \qquad (3.4)$$

Where the volume of desorbed solution (L) is V_d, C_d is the metal ions concentration in desorbed solution (mg/L), W is the weight of adsorbent used for desorption studies (g) and q_e is the adsorption capacity of metal ions adsorbent.

3.4.4 Experimental Design

An experimental layout was designed by varying different parameters. This was used as a guideline for the batch adsorption-desorption studies. Table 3.1 shows the experimental design for this study. The concentration of Cd (II) ion was initially fixed to 2 mg/L.

Table 3.1 Experimental parameters varied in batch adsorption-desorption studies

Adsorbent dose (g/L)	Contact time (min.)	pH	Agitation speed (rpm)	Cd initial concentration (mg/L)	Temperature (K)
0	0	4	50	1	273
1	15	5	100	2	288
2	30	6	150	5	298
3	60	7	200	7	308
4	120	8	250	10	318
5		9			328
6		10			

3.5 Adsorption Isotherm Models

The description of adsorption behavior is usually provided by mathematical models known as the adsorption isotherm models (Al-Khaldi et al., 2015). The distribution of adsorbate

molecules between the liquid phase and a solid phase at equilibrium state can be indicated by the adsorption isotherm (Asmaly et al., 2016). In this study, Langmuir, Freundlich, and Scatchard isotherm model were employed to access the adsorption behavior of polyelectrolyte-coated fly ash $(PEFA)_{20}$ and $(PEFA)_5$ for Cd (II) ion removal in an aqueous medium.

3.5.1 Langmuir Isotherm

Langmuir isotherm model explain the monolayer adsorption, suggesting that adsorbent materials have finite capacity, regarded as the equilibrium state which is the point beyond which no further adsorption takes place (Langmuir, 1918). The existence of specific homogeneous sites within the adsorbent at which adsorption occurs is it main assumption (Ihsanullah et al., 2015). The Langmuir isotherm is expressed by the equation (3.5) below:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{3.5}$$

The above equation can be linearized to

$$\frac{1}{Q_e} = \frac{1}{Q_{max} K_L C_e} + \frac{1}{Q_{max}} \tag{3.6}$$

From the equation above, C_e is the equilibrium of Cd (II) concentration (mg/L); Q_e is the amount of Cd (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); Q_{max} is the theoretical maximum adsorption capacity (mg/g) and K_L is the Langmuir isotherm constant (L/mg). A linear plot of $\frac{1}{Q_e}$ against $\frac{1}{C_e}$ can be used to obtain the values of Q_{max} and K_L from slope and intercept respectively. The important features of Langmuir parameters can be

applied to further forecast the interaction between the adsorbate and adsorbent with the aid of dimensionless separation parameters (R_L) as indicated in equation 3.7 below:

$$R_L = \frac{1}{1 + K_L C_i} \tag{3.7}$$

Where K_L is Langmuir constant and C_i is Cd (II) ions initial concentration. R_L value gives essential information on sorption nature. If the R_L= 0, then the reaction is irreversible, the reactions is favorable if R_L> 0 but >1 i.e. ($0 < R_L > 1$), the reaction is linear if $R_L = 1$ while the reaction becomes unfavorable if $R_L < 1$.

3.5.2 Freundlich Isotherm

The Freundlich isotherm model (Freundlich, 1906) also explains the adsorptive behavior of the adsorbent material. Adsorption on the heterogeneous surface with the interaction between adsorbate molecules being the main application of this model (Rathod et al, 2015). The Freundlich isotherm can be expressed by the equation 3.8 below:

$$Q_e = K_f {C_e}^{1/n} \tag{3.8}$$

The above equation can be linearized to

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3.9}$$

From the equation above, C_e is the equilibrium of Cd (II) concentration (mg/L); Q_e is the amount of Cd (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); K_f is the Freundlich adsorption constant related to the adsorption capacity [(mg/g) (L/mg)]. A linear

plot of ln Q_e against ln C_e can be used to obtain the values of K_f and n from intercept and slope respectively.

3.5.3 Scatchard Isotherm Model

The Scatchard isotherm model is the modification of conventional Langmuir equation and it is commonly used to study the features of the sorption process, as it simplifies isotherm descriptions. It offers a comprehensive understanding of the binding site affinity. This model can also be known as the independent site oriented model. It can be expressed by equation 3.10 below (Scatchard, 1949).

$$^{Q_e}/_{C_e} = Q_s b - Q_e b \qquad (3.10)$$

Where Q_s and b are the constants for Scatchard isotherm expressed in mg/g and L/mg respectively. A linear plot of $^{Q_e}/_{C_e}$ against Q_e can be used to obtain the values of Q_s and b from intercept and slope respectively. The Scatchard plot shape is associated with the category of interaction of the solute phase (Henis & Levitzki, 1976). A nonconforming linearity of this kind of plot frequently specify the existence of multiple binding sites while a conformed linear plot identify an identical binding site that is independent. Consequently, if the Scatchard plot has a negative slope and is linear, then it follows the Langmuir model by confirming the interaction between metal ion solution and adsorbent binding sites (Anirudhan & Suchithra, 2010). One worthwhile aspect that give the Scatchard plot edge over other isotherm models is that it's provide detailed information on the nature of active sites (Küçükosmanoğlu et al, 2006; Dawodu et al, 2012).

3.6 Kinetic Studies

The adsorption of Cd (II) was analyzed using different kinetic models like pseudo-first order (equation 3.11) (Lagergren, 1898), pseudo-second order (equation 3.12 & 3.13) (McKay et al, 1999), and weber intra-particle diffusion (equation 3.14) (Weber, 1972) expressed in the equations below:

$$\log\frac{(q_e - q_t)}{q_e} = \frac{-K_L t}{2.303} \tag{3.11}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e + Kt} \tag{3.12}$$

$$\frac{t}{q_t} = \frac{1}{(2K_s {q_e}^2)} + \frac{t}{q_e} \tag{3.13}$$

$$q_t = K_{id} t^{1/2} + C \tag{3.14}$$

From the equation above q_e and q_t are amounts of Cd adsorbed (mg/g) at equilibrium and at a given time, t (min) respectively. K_L is the pseudo-first order rate constant sorption (min^{-1}). K_s and K are pseudo-second order and second order adsorption rate constants ($g.mg^{-1}.min^{-1}$). K_{id}, $t^{1/2}$ and C are intra-particle diffusion rate constant ($mg/g.\ min^{-1}$), square root of time $(min)^{1/2}$, and intercept respectively. The constants (K_L, K_s and K) can be determined from the slopes of linear plots of $\log(q_e - q_t)$ against t, $\frac{t}{q_t}$ against t and $\frac{1}{(q_e - q_t)}$ against t, where q_e can be determined from the intercept data of pseudo-second order and second order rate equations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material Characterization

Characterization tests were conducted to identify elemental, phase, functional groups as well as the thermal ability of the adsorbent materials (RFA, AFA, PEFA). The results of the characterization obtained from the various techniques are given in the paragraphs below.

4.1.1 Field Emission Scanning Electron Microscopy (FESEM)

The micrograph (Figure 4.1) obtained from the FESEM shows that RFA has hollow shape with heterogenous pore structures. The diameter of the RFA used for this study varies from 50-500 micron with an average diameter of 100 microns having surface pores of varying sizes. Figure 4.1 display FESEM micrographs of RFA at 382x and 1.27kx magnifications confirming that the adsorbent is spherical, mesoporous (2 to 50 nm), dispersed and heterogenous pore sizes. Figure 4.2 on the other hand, shows FESEM micrographs of AFA with spherically dispersed, mesoporous and some cracked structures due to acid treatment of the fly ash. As shown in Figure 4.3, PEFA micrographs obtained shows similar morphology to AFA and RFA and a thin pore linen indicated in red was seen due to coating with PDADMAC-PSS.

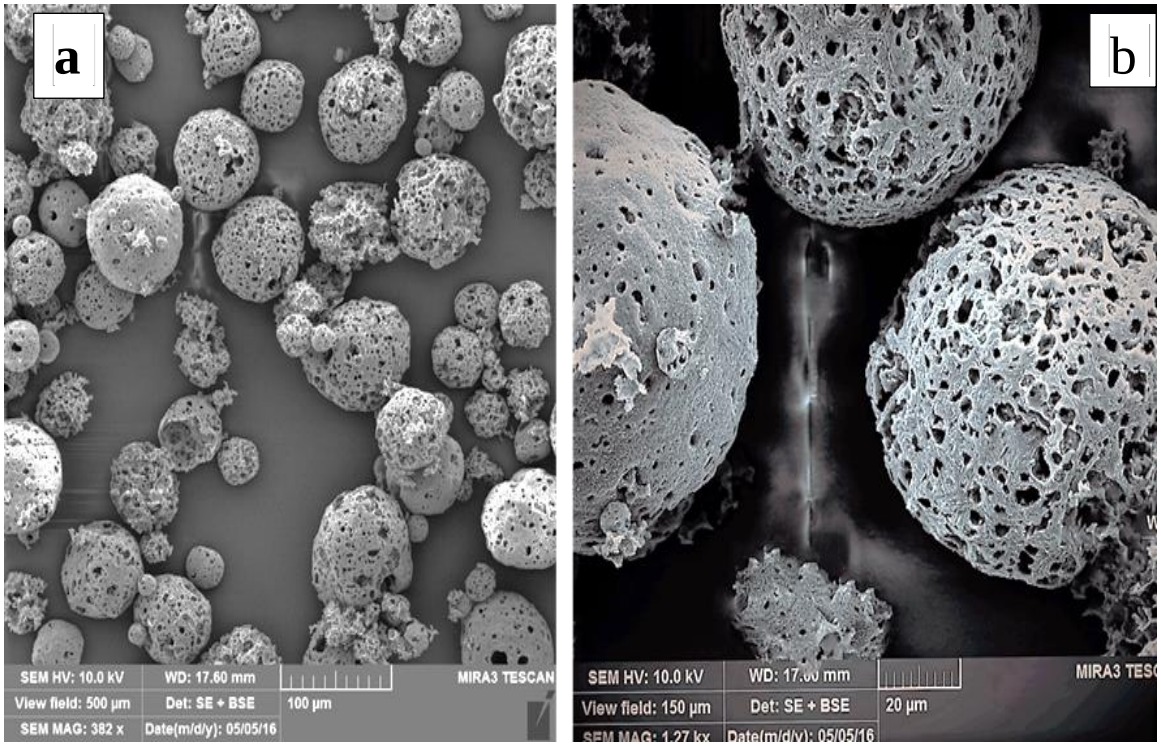

Figure 4.1 FESEM micrographs of RFA viewed at (a) 382 x (b) 1.27 kx magnification

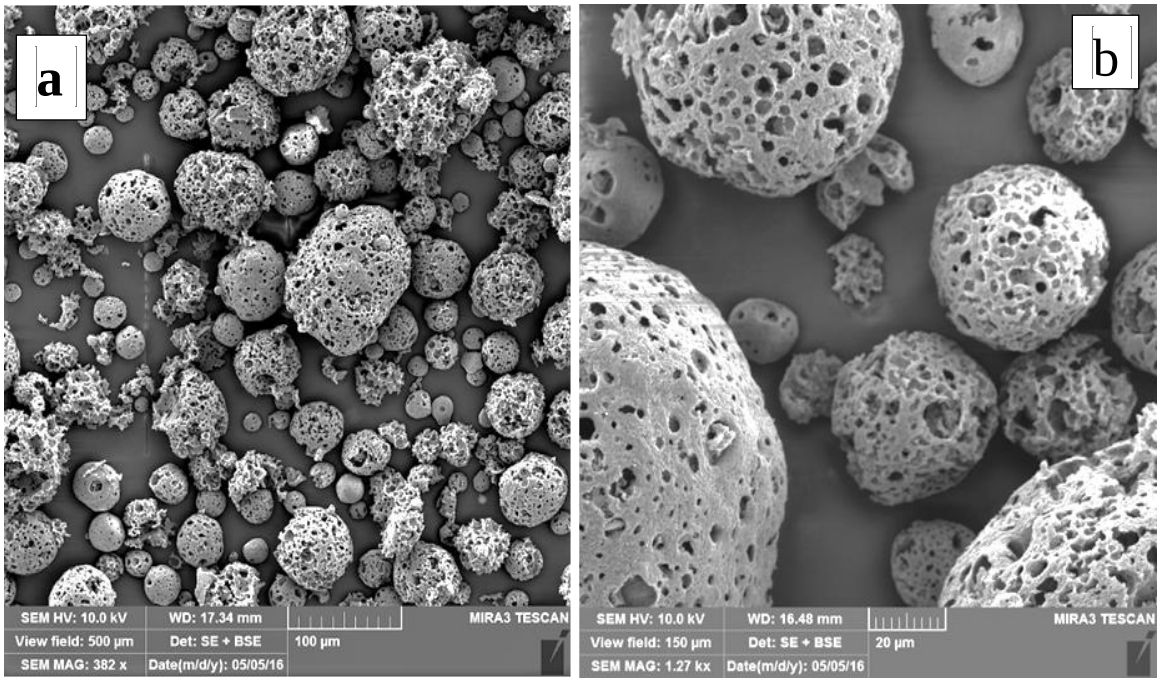

Figure 4.2 FESEM micrographs of AFA viewed at (a) 382 x (b) 1.27 kx magnification

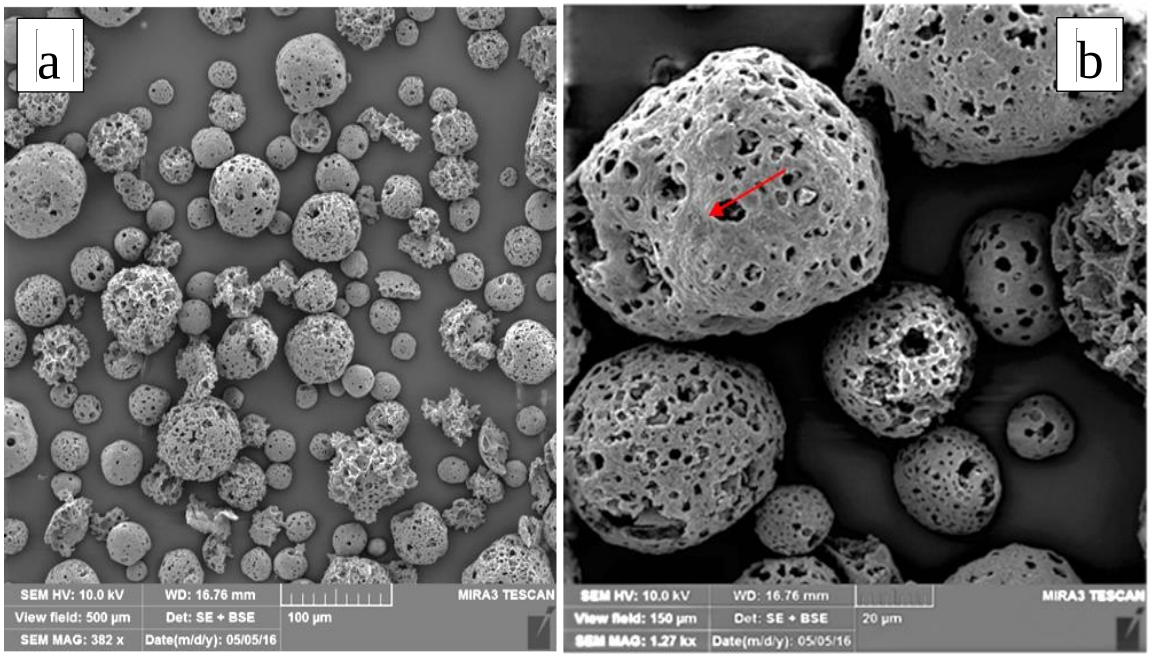

Figure 4.3 FESEM micrographs of PEFA viewed at (a) 382 x (b) 1.27 kx magnification

4.1.2 Energy Disperse X-ray Spectroscopy (EDXS)

The microchemical spot analysis of the prepared adsorbents (RFA, AFA, and PEFA) were also investigated with EDX spectroscopy. The EDX spectra obtained from this analysis as shown in Figure 4.4 indicates that RFA contain mainly of carbon with 71.7 % composition, and oxygen at 16.6 %, in addition to this there were elements like silicon, copper, vanadium, aluminium and sulphur with 0.2, 6.0, 0.7, 2.0 and 2.8 % respectively. However, Figure 4.5 shows that there was an increase in carbon composition from 71.7 to 91.0 % and increased silicon content from 0.2 to 0.4 %. Moreover, comparing the EDX spectra of Figure 4.5 to that of spectra in Figure 4.4, there was no appreciable levels of impurities like heavy metals as a result of acid treatment of RFA. This was essential to ensure there was no metal impurities like Cu, Cd, Mn, Vn, Ni etc. to avoid cross contamination of sample during adsorption study. Additionally, Figure 4.6 confirms the presence of polyelectrolyte as there was an increase in sulphur content from 2.8 to 5.0 % due to the presence of polymer that has a Styreno-sulfonate compound (i.e PSS) in its composition.

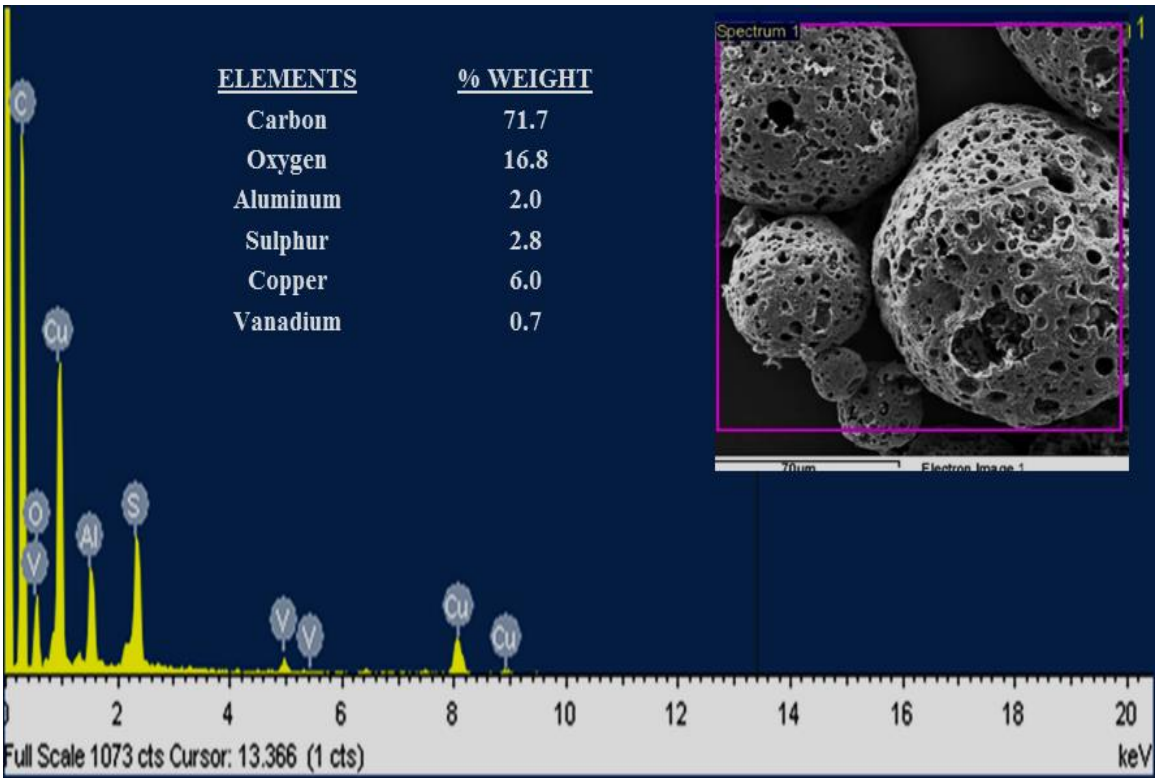

Figure 4.4 EDX spectrum of raw fly ash (RFA)

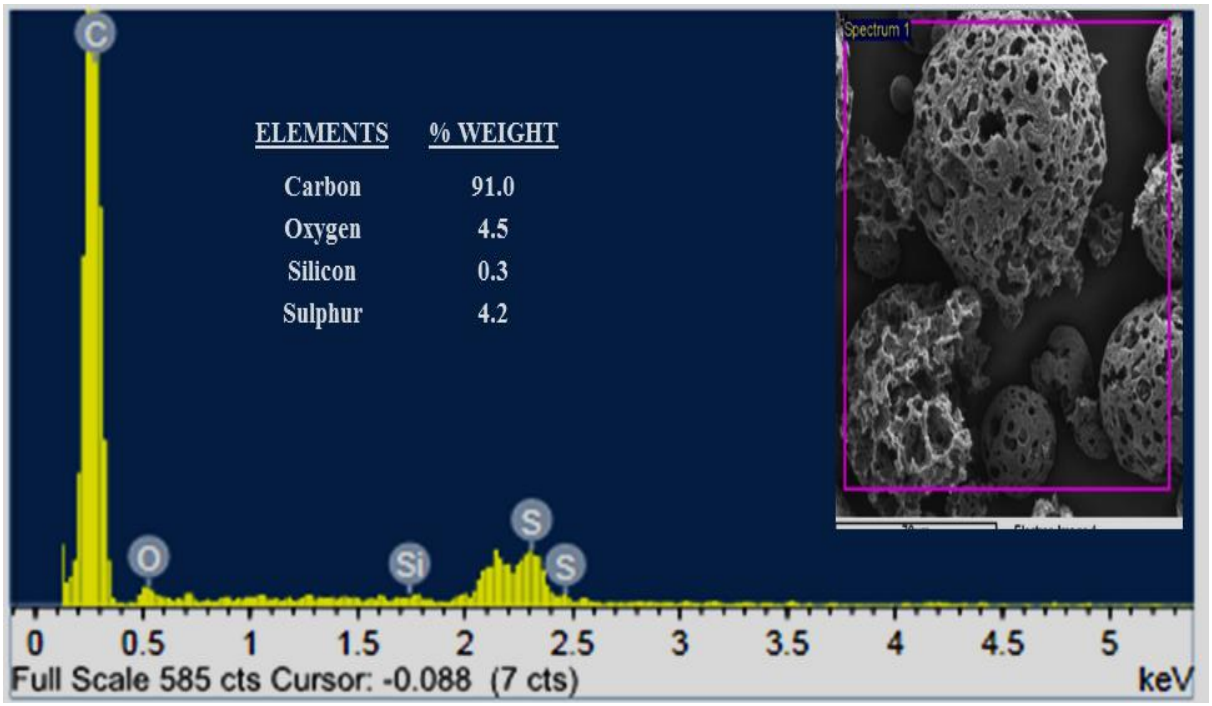

Figure 4.5 EDX spectrum of acid treated fly ash (AFA)

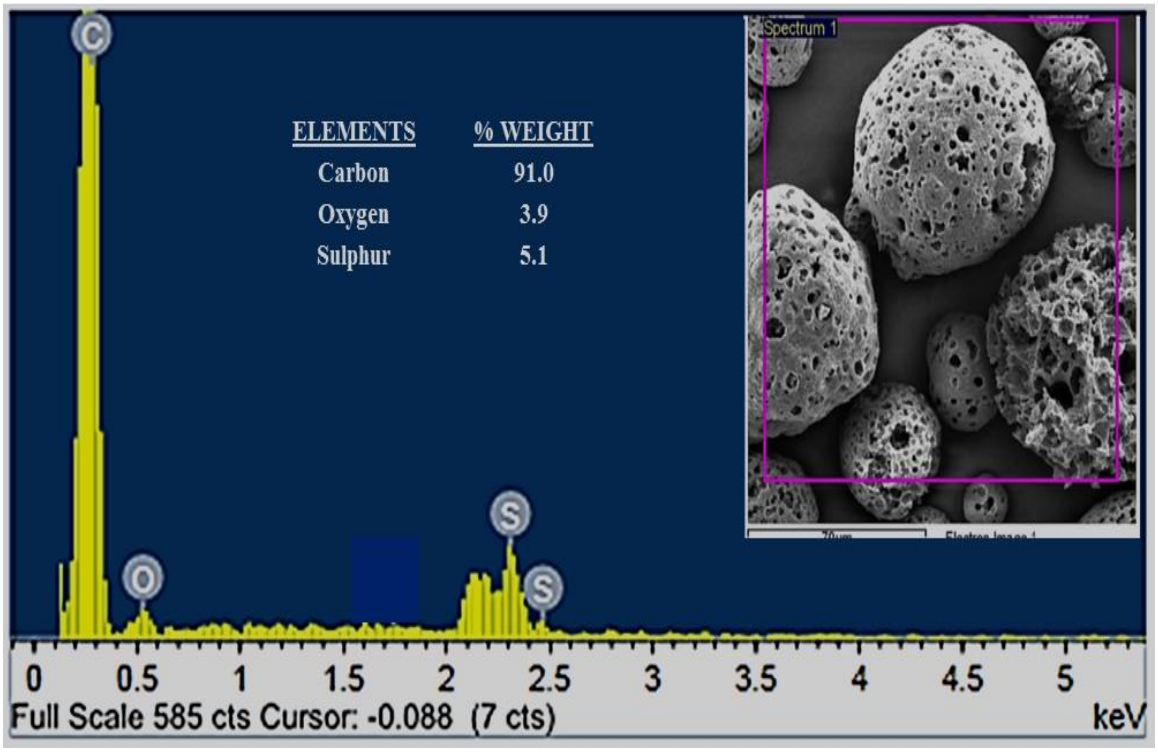

Figure 4.6 EDX spectrum of polyelectrolyte-coated fly ash (PEFA)

4.1.3 Elemental Analysis by X-ray Fluorescence (XRF)

XRF analysis was carried out to determine the elemental composition of the AFA and PEFA adsorbents. The results as summarized in Table 4.1 identified the presence of some trace metals like vanadium, manganese, iron, nickel, zinc, and molybdenum with their percentage compositions. It was observed that RFA has no silicon content, sulphur was high at 51% composition which could be attributed to the fact that the fly ash is an oil fly ash usually characterized with low silicon and aluminium contents (Al-Degs, et al, 2014(Vitolo et al, 2000). As could be inferred from the EDX spectrum the fly ash has a high carbonaceous content which is not commonly found at that rate in coal fly ash with high silicon and aluminium contents (Wang et al., 2011; Pires & Querol, 2004). After treatment with acid (AFA), the fly ash trace metal content was reduced to a non-significant form whereas sulphur content increased from 51% to 86% as shown in the table below. In PE-FA, trace metals were neither presence nor in appreciable level but sulphur content increases to 92.5% which might be as a result of addition of sulphate group present in the polymer used for coating.

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR technique was used to ascertain the functional groups present in RFA, AFA, and PEFA surface. The samples were scanned from 500-4000 cm^{-1} and the intensity of peaks in the IR spectra was observed. Figure 4.7 shows FTIR spectra for RFA, AFA and PEFA. The raw fly ash shows a mildly prominent peak at 604 cm^{-1} as a result of the naturally occurring C-S bond (Coates, 2000). There was a prominent peak at 1367 cm^{-1} as a result of skeletal vibration of a C-C bond (Parvez et al, 2014). A peak was observed at 1628 cm^{-1} which indicates the presence of C=C functional group of an alkene (Shawabkeh et al.,

2012). A sharp peak at 1711 cm^{-1} represents C=O in ester group as noted by Shawabkeh et al., 2011. A broad trough was observed at 3436 cm^{-1} as a result of O-H stretching of alcoholic groups (Shawabkeh et al., 2011; Jiang et al, 2008). However, after treating with an acid (HNO_3), peaks were only seen at lower and higher region of the spectra, this might be as result of the bond breaking due to reactions between the acid and fly ash particles. After coating the AFA with polyelectrolytes (PDADMAC & PSS), a more prominent and sharp peak was observed at 607 cm^{-1} of PEFA which is evident of the presence of more C-S functional group. The peak of C=C reappeared at 1635 cm^{-1} (Abuilaiwi et al., 2010; Rathod et al., 2015). Additionally, there was C-N peak at 2386 cm^{-1} which indicate the presence of the polyelectrolytes PDADAMAC on the fly ash (Guo et al, 2013; Wang et al., 2011). The peaks observed at 3442 and 3451 cm^{-1} of the RFA and AFA spectra respectively were also observed at 3454 cm^{-1} in PEFA indicating the presence of carboxylic acid O-H functional groups.

4.1.5 Phase Identification by X-ray Diffraction

The phase analysis of RFA, AFA, and PEFA was studied using X-ray diffractometer. Overall, the XRD spectra in Figure 4.8 show the presence of carbon, sulphur, α-quartz (low quartz content), β-quartz (high quartz content) and cristobalites. A prominent peak was observed between at 2Θ of 21.6^o, this confirms the presence of highly concentrated carbon of graphite. The amorphous phase between 2Θ of 22^o and 28^o contain sulphur and quartz respectively. β-quartz at 2Θ of 27.4^o was present in both AFA and PEFA as compared to α-quartz in RFA because impurities trace metals embedded on the surface of RFA has been removed through acid treatment, this bring about the existence of more silicon content in the AFA and PEFA. No significant peaks were observed after 2Θ of 40^o indicating the

presence of amorphous carbon. The XRD pattern of this material can be attributed to that of carbon black or oil fly ash which are both amorphous. Also, the crystalline structure of oil fly ash is known to consist of carbon and metallic sulphur in the amorphous state (Kwon et al, 2005).

4.1.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed to measure the thermal stability and purity of adsorbents. Figure 4.9 displays the thermograms of RFA, AFA, and PEFA. All samples analyzed exhibit similar curves and do not contain adsorbed water. Due to volatilization/decomposition of organic or inorganic substances, a 2% weight loss was observed between 100-470 ^{o}C in RFA. Dramatic weight losses of 84% for RFA between 470 -600 ^{0}C, 80% for AFA at temperature range 580 – 630 ^{0}C), and 97% for PEFA between 580 – 670 ^{0}C can be attributed to the phenomenon of gas generation (CO_2 and CO) upon pyrolysis (Zou et al., 2013). Among the three adsorbents, AFA seems to be more thermally stable than the rest with a residual of approximately 5%. Other samples burn off almost completely before the maximum set temperature of 900 ^{0}C.

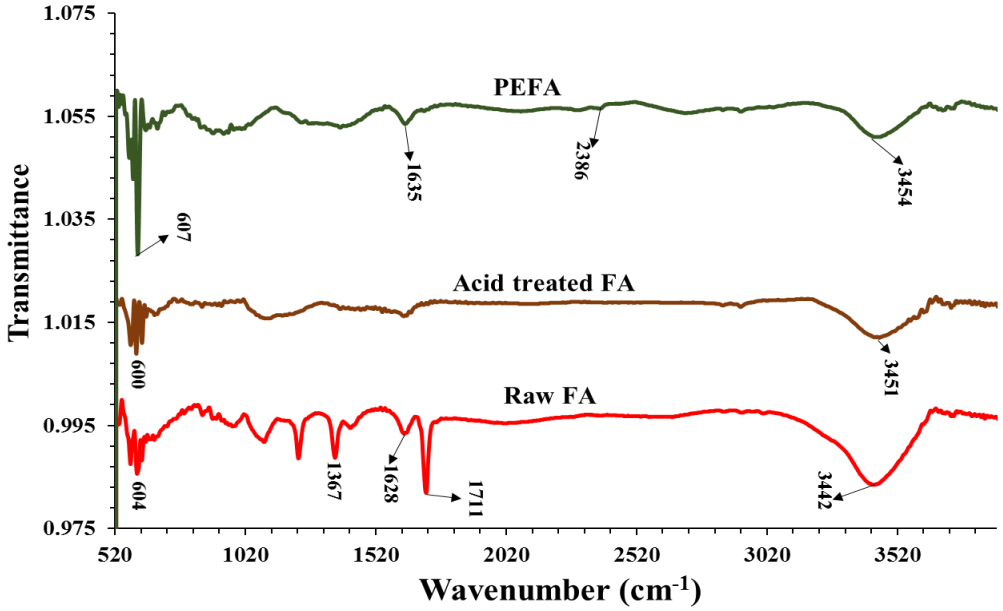

Figure 4.7 IR-spectra of RFA, AFA and PEFA

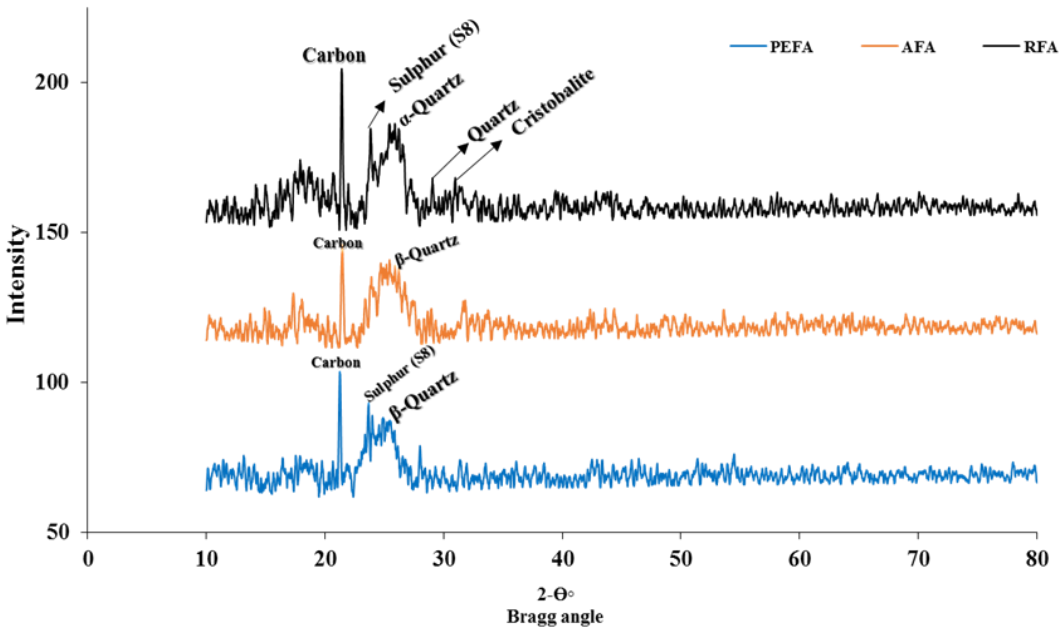

Figure 4.8 XRD-spectra of RFA, AFA and PEFA

Table 4.1 Elemental composition of RFA, AFA and PE-FA as revealed by XRF (% Weight)

Atomic number	Elements	RFA	AFA	PEFA
14	*Silicon*	0	0.76	0.00
15	*Phosphorus*	1.09	0.66	1.18
16	*Sulphur*	51.44	86.25	92.50
20	*Calcium*	1.91	2.16	2.23
23	*Vanadium*	20.22	5.10	1.09
25	*Manganese*	0.10	0.00	0.00
26	*Iron*	11.34	2.10	1.29
28	*Nickel*	13.46	2.95	1.70
30	*Zinc*	0.41	0.00	0.00
42	*Molybdenum*	0.02	0.01	0.00
	Loss on Ignition	0.01	0.01	0.01
	TOTAL	**100**	**100**	**100**

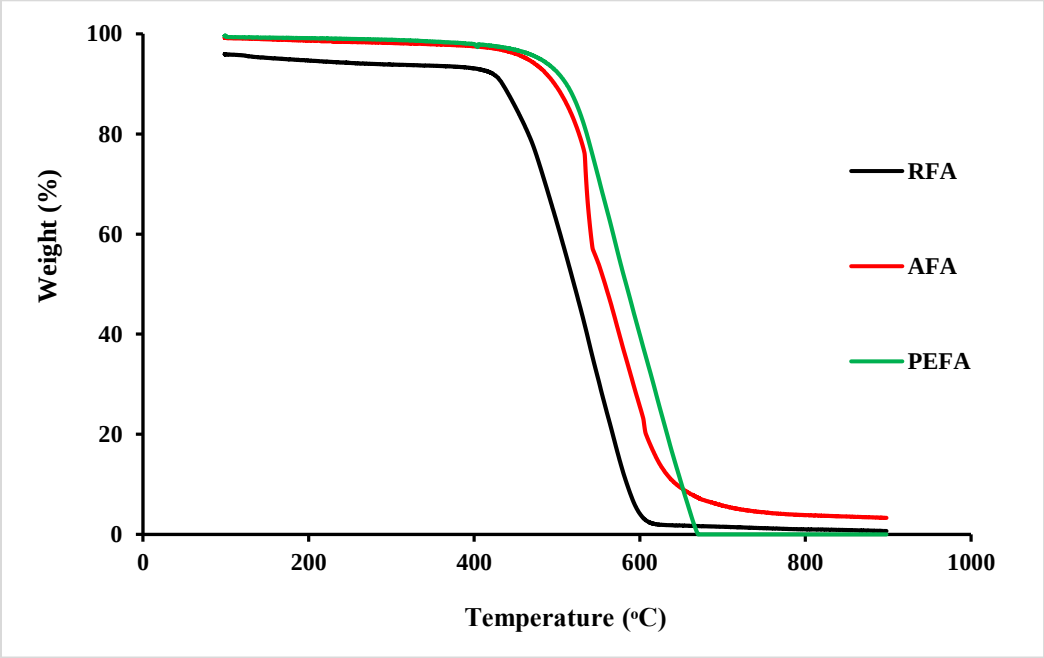

Figure 4.9 Thermogram for RFA, AFA, PEFA

4.2 Removal of Cd (II) using PEFA Adsorbent

One of the main objectives of this study was to apply the prepared adsorbent to remove Cd (II) from contaminated water through batch adsorption studies. With much focus on the polyelectrolyte based adsorbents $(PEFA)_5$ and $(PEFA)_{20}$), Cd (II) ion sorption onto the surface of the adsorbents was evaluated based on percent removal each period of contact. The effects of various experimental parameters which includes pH, contact time, dose of adsorbents, mixing rate, initial concentration of Cd (II) ion, temperature and number of layers. Results of this part of the study are presented and discussed in the paragraphs below.

4.2.1 Effect of pH

Generally, metal adsorption consist of a multifaceted mechanism of ion exchange, metal chelating with numerous anion functional groups, physical forces sorption and trapping of ions in the interior sphere of adsorbents architectural network (Kovo et al, 2015). Different forms of Cd species occurs in deionized water as Cd (II), $Cd(OH)_{2(s)}$, $Cd(OH)^+$ (Leyva-Ramos et al, 1997). The pH was a leading factor affecting Cd (II) ion removal under the investigated conditions. Nonetheless, Cd (II) often exist as a complex $[Cd(H_2O)_6]^{2+}$ at low pH and also a prevailing species (Ihsanullah et al., 2015). With specific focus on PEFA, the adsorption of Cd (II) ions by RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$ were investigated to fix the optimum pH removal. With 4 g/L dosage of the adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$), mixing rate of 150 rpm, 2 mg/L of metal ion concentration, contact time of 15 minutes and at 298 k temperature, batch experiment was conducted for pH values 4 to 10. Figure 4.10 illustrate an increase in Cd (II) removal efficiency with an increased pH in aqueous solution. Maximum sorption of Cd (II) ion was attained at pH 7 and 9 due to the

fact that in acidic medium Cd (II) ion sorption is low because bulky amounts of proton (H^+) compete with Cd (II) ions for active sites but as the pH increases, the number of positively charge ions available for active sites reduces with a rise in negatively charged ion for binding (Rathod et al., 2015). Though at pH greater than 4, precipitation of metal ions may occur as an OH^- (K.G. Akpomie & Dawodu, 2015). As observed by (Akpomie & Dawodu, 2015) that precipitation may accounts for metal ions sorption at higher pH. In order to quantify the amounts of Cd (II) ions precipitated, aqueous solution of Cd (II) at the studied pH were investigated under similar conditions for 15 minutes, precipitation percent was then calculated by equation 4.1:

$$\%\ Precipitation = \frac{C_i - C_e}{C_e} \times 100 \qquad (4.1)$$

Where C_i and C_e are the initial and equilibrium of Cd (II) ions concentrations (mg/L) in the aqueous solution respectively. % precipitate was shown on the graph in Figure 4.10 as control.

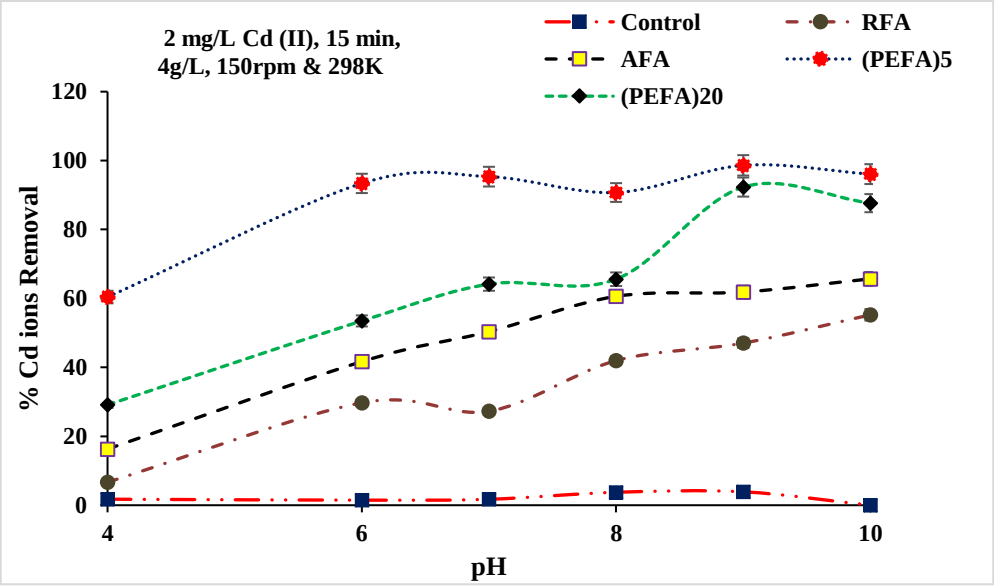

Figure 4.10 The effect of pH on the percent removal of Cd (II) ions on FA based adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)

4.2.2 Effect of contact time

Contact time is the time required for equilibrium to be attained in the process of adsorption when no substantial variations were detected in adsorptive concentration after a definite period of time (Rathod et al., 2015). It hinges on the surface features of the adsorbent in question. To find the optimum contact time for Cd (II) ions uptake, varying contact time from 5 minute to 2hrs were studied from aqueous solutions of 2 mg/L Cd (II) ions concentration, adsorbent mass of 4g/L, pH value of 7, mixing rate of 150 rpm and 298 k temperature. The results gotten indicated that at first there was rapid adsorption of Cd (II) ions for $(PEFA)_5$ and $(PEFA)_{20}$ with 97 and 78 % removal respectively and a gradual decrease to attain equilibrium in 2hrs as shown in Figure 4.11. Initial fast adsorption for this adsorbent might be as a result of rich active sites on the adsorbent surface which becomes filled up with increased time and turn out to be saturated (Akpomie & Dawodu, 2015; Akpomie et al., 2015; Rathod et al., 2015; Li et al., 2003). For this study, optimum contact time was chosen to be 15 minute as maximum Cd ions removal was reached at this time. As for RFA and AFA there was 30 and 57% removal respectively at optimum contact time.

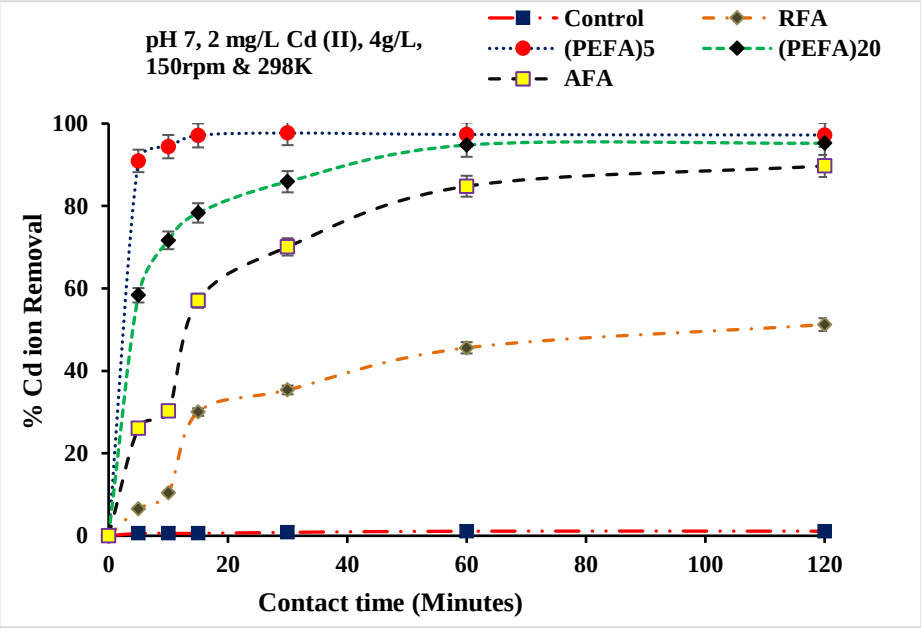

Figure 4.11 The effect of contact time on the percent removal of Cd (II) ions on FA based adsorbents ((RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$))

4.2.3 Effect of adsorbent dosage

The mass of adsorbent has effect on the active site available for binding of Cd (II) ions in aqueous solution(Gupta & Torres, 1998; Asmaly et al., 2016). In this study, batch mode experiment was conducted by applying varying quantities of (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$) from 1 to 6 g/L at pH value of 7, 2 mg/L, 150 rpm mixing rate, 50 ml volume aqueous solution and 298 K temperature. As illustrated in Figure 4.12, Cd (II) ion sorption rises with increase in dose of adsorbents up till 4 g/L and there was little or no significant adsorption for remaining dosage. Sorption increase with an increase in dose of adsorbent could be attributed to surface area increase, rise in the exchange site ability of the ion, and an increase in active sites (Gupta & Torres, 1998; Ali, 2014). $(PEFA)_5$ reach optimum at 4 g/L with percent removal of over 97 % as compared to $(PEFA)_{20,}$ RFA and AFA with 78,

57 and 31 % removal efficiency respectively. Incomplete adsorbent aggregation which leads to a decline in Cd ion uptake active surface area may be the reason for drop in removal efficiency of at higher concentration for RFA and AFA. 4g/L adsorbent dose was used for other investigation.

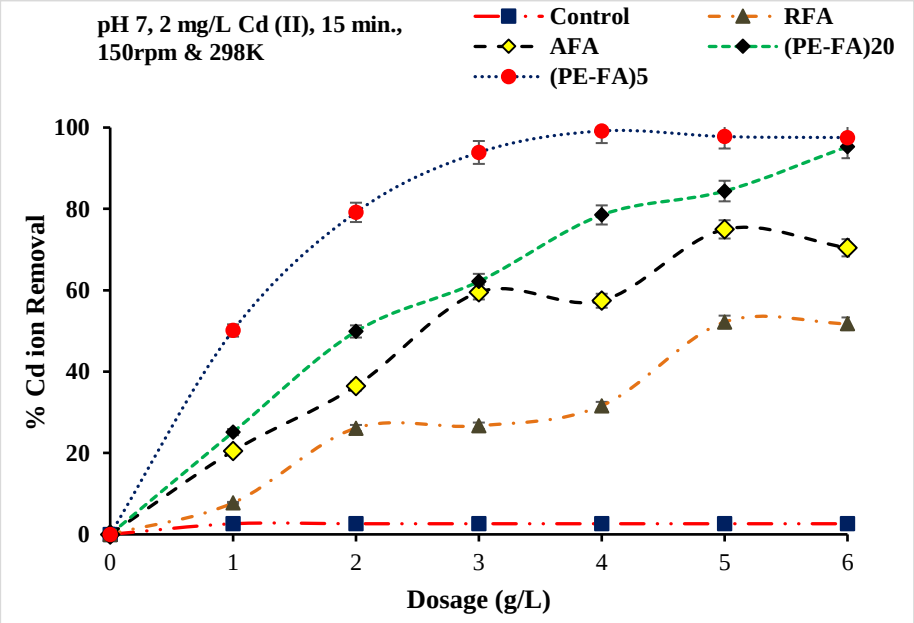

Figure 4.12 The effect of adsorbent dose on the percent removal of Cd (II) ions on FA based adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)

4.2.4 Effect of mixing rate

The mixing rate ensures that Cd (II) ions are transferred to the active sites by supporting the contact between Cd ions in aqueous solution and adsorbent binding sites (Papandreou et al, 2007; Ali, 2014). The optimum removal of Cd (II) at pH value of 7 was used to investigate the effect of mixing rate on the adsorption of Cd (II) ion for ((RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)). Figure 4.13 indicates that the removal of Cd (II) ion increases with mixing rate increase from 50 to 150 rpm. Maximum removal of over 96 % was

achieved for $(PEFA)_5$, followed by $(PEFA)_{20}$ with 84 % as well as 7 AFA and RFA with 53 and 28 % respectively at 150 rpm with 2 mg/L metal ion concentration, 50 ml volume of aqueous solution, 4 g/L dose of adsorbents, pH value of 7, contact time 15 minutes and 298 K temperature. Afterword there was no significant removal achieved above this mixing rate under similar conditions. This observation could be ascribed to improved interaction between the sorption active sites and Cd (II) ions in aqueous solution with an increase mixing rate (El-sherif & Fathy, 2013). 150 rpm was chosen as optimum mixing rate due to removal efficiency at this rate and applied for further investigation.

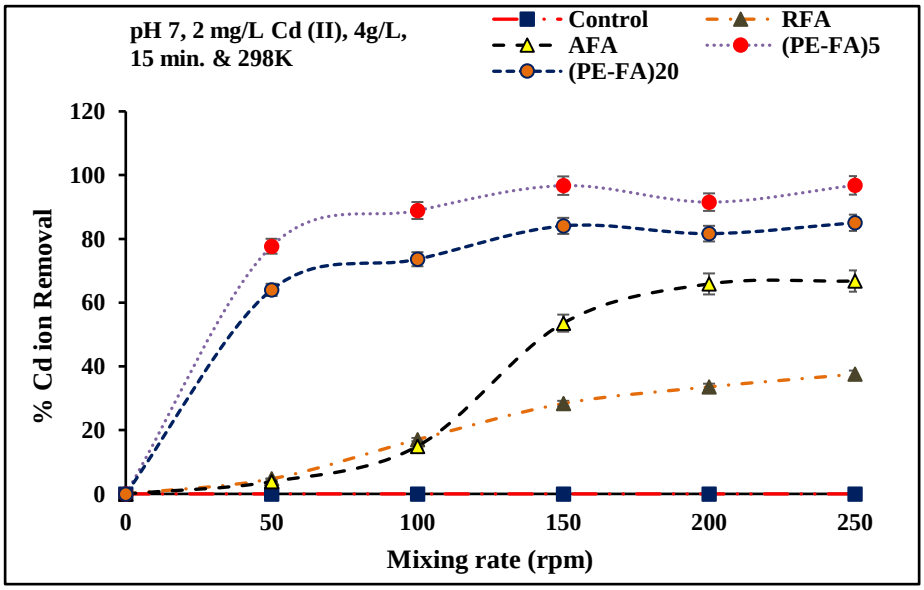

Figure 4.13 The effect of mixing rate on the percent removal of Cd (II) ions on FA based adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)

4.2.5 Effect of initial concentration

Investigating the initial concentration of metal ion is very essential in the sorption studies because water and wastewaters contamination do have diverse metal ion concentrations, hence, knowledge of its influence is required for an elaborate sorption investigation (Gupta et al, 2003; Akintola et al, 2016). The effect of Cd (II) ion concentration in aqueous solution on its sorption by was conducted at optimum conditions of 4 g/L dose of adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$), pH value of 7, 150 rpm mixing rate, 15 min contact time and 298 K temperature. Initial Cd (II) ions concentration investigated were varied from 1 to 10 mg/L and its effects on the removal efficiency was established. In Figure 4.14, it was observed that increasing the initial concentration of Cd (II) ions in solution could cause a decline in the removal efficiency of RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$. Though $(PEFA)_5$ perform better than other investigated adsorbents with 68 % removal for 10mg/L as compared to 42 % in $(PEFA)_{20}$. This can be ascribed to bulky quantities of Cd (II) ion with inadequate active sites on the surface of the adsorbents which resulted in increased concentration of Cd (II) ion in the greater part of the aqueous solution and as a result decreasing Cd (II) ion removal (Hegazi, 2013).

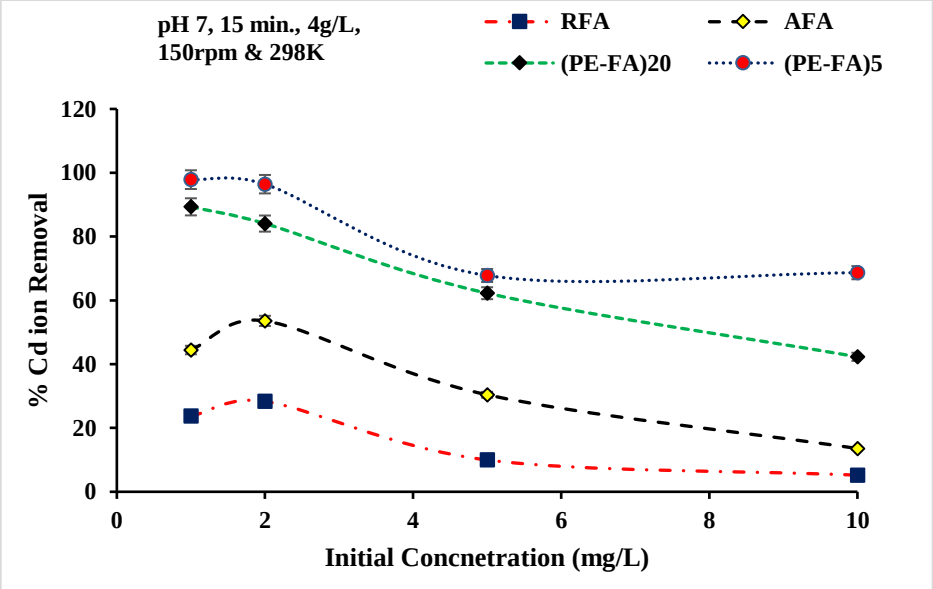

Figure 4.14 The effect of initial concentration on the percent removal of Cd (II) ions on FA based adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)

4.2.6 Effect of temperature

Figure 4.15 illustrates Cd (II) ion sorption on RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$ at different temperatures. It can be deduced from the graph that a rise in temperature brings about a sharp increase in Cd (II) sorption from 273-298 K (Veličković et al., 2013 ; Catena & Bright, 1989). This observation could be attributed to the fact that more sites are present as temperature rises from 288-298 K to surface component dissociation on PEFA. This also suggests that the physical sorption mechanism may have played a role in Cd (II) ion removal by the surface of PEFA. As the temperature increases from 308- 328 K Cd (II) ions adsorption increases as well, this increase suggests that high temperature might be favorable factor in the sorption process as well and gives the indication that the adsorption is endothermic.

To assess the feasibility and spontaneity of sorption process, thermodynamic parameters like ΔG^o (free energy change), ΔH^o (enthalpy change) and ΔS^o (entropy change) were determined as shown in table 4.2. Gibb's free energy change of sorption was calculated from equation 4.2 below;

$$\Delta G^o = -RT \ln K_d \qquad (4.2)$$

Where R (8.314 J/mol. K), T (K) is the absolute temperature and K_d is the distribution coefficient expressed as $K_d = \frac{q_e}{C_e}$ where q_e is the amount of Cd (II) ion adsorbed at equilibrium and C_e is the concentration of Cd (II) ion in aqueous solution at equilibrium.

$$\ln K_d = -\frac{\Delta G^o}{RT} \qquad (4.3)$$

$$\ln K_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (4.4)$$

Equation 4.4 is known as the Van Hoff equation, the values of ΔH^o and ΔS^o were calculated from slope and intercept of the plot of $\ln K_d$ against T^{-1} (K^{-1}) as indicated in Figure 4.16.

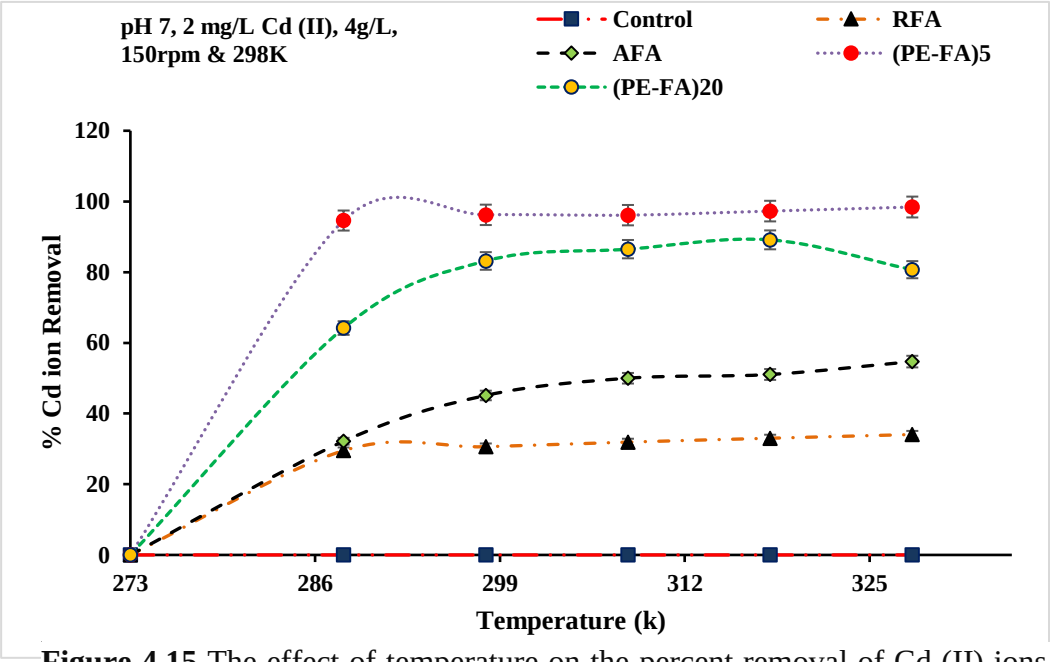

Figure 4.15 The effect of temperature on the percent removal of Cd (II) ions on FA based adsorbents (RFA, AFA, $(PEFA)_5$ and $(PEFA)_{20}$)

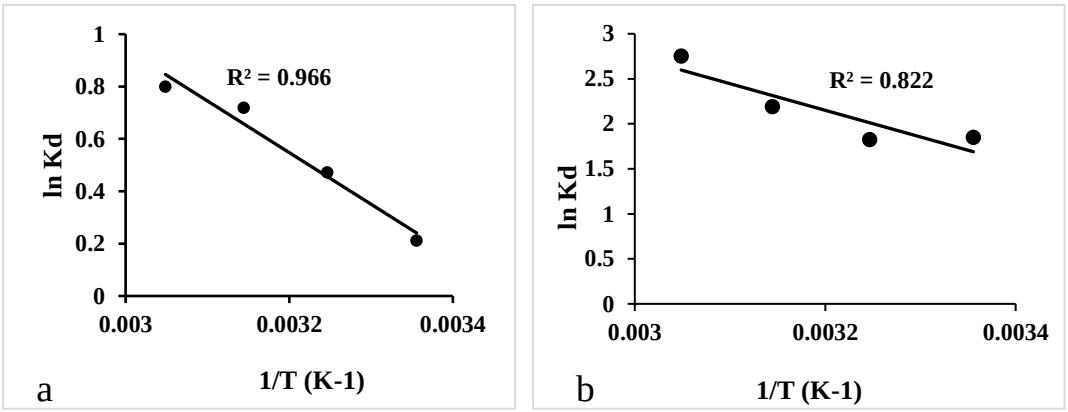

Figure 4.16 Van Hoff plot for Cd ion sorption. a) $(PEFA)_{20}$, b) $(PEFA)_5$

Table 4.2 Thermodynamic parameters for Cd (II) ions adsorption by polyelectrolyte coated fly ash (PEFA)

Number of PEFA Layers	T (k)	Kd (L/g)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
5	298	6.4	-4.6	22.4	89.8
	308	6.2	-4.7		
	318	8.9	-5.8		
	328	15.6	-7.5		
20	298	1.2	-0.5	16.4	57.0
	308	1.6	-1.2		
	318	2.1	-1.9		
	328	2.2	-2.2		

The values of standard enthalpy changes ΔH^o (KJ/mol), standard entropy ΔS^o (J/mol/K), and Gibbs free energy ΔG^o (KJ/mol) calculated for this study are presented in Table 4.2. The coefficient of distribution (K_d) increases with an increase in temperature, as this may be ascribed to the fact that there is enhancement of the intra-particle diffusion rate and a rise in pore sizes as well (Bhattacharyya & Gupta, 2006). This observation can be seen in table for both $(PEFA)_5$ and $(PEFA)_{20}$ respectively. The values for ΔG^o (Gibbs free energy) are negative, which implies that the sorption was driven by greater force and ascertained the spontaneity of Cd (II) ions sorption onto the surfaces of $(PEFA)_5$ and $(PEFA)_{20}$, as well as a thermodynamically favorable condition. There was positive ΔH^o values for both $(PEFA)_5$ and $(PEFA)_{20}$, this implies that the adsorption process is endothermic in nature and also the level of ΔH^o can be used to determine the adsorption type as well. If the level is in the between 2.1-20.9 kJ/mol, this signify physiosorption mechanism, while a chemical adsorption process falls between 80-200 kJ/mol. The value of ΔH^o obtained in this investigation for both $(PEFA)_5$ and $(PEFA)_{20}$ indicates a physiosorption process. Inclusively, values of ΔS were positive as well, which indicates there is affinity between the adsorbent and increase in randomness at the surface of the adsorbent during sorption process. The magnitude of ΔS^o can also be used to signify whether the sorption reaction is associative or dissociative, if the value is greater than -10 J/mol/K, it implies that the sorption fit into dissociative mechanism (Meitei & Prasad, 2013). Therefore, ΔS values obtained in this study indicates that the sorption of Cd (II) ions onto $(PEFA)_5$ and $(PEFA)_{20}$ fit dissociative mechanism, as the values gotten were much larger than -10 J/mol/K.

4.2.7 Effect of number of layers

The influence of PEFA layers on Cd (II) ions sorption was investigated to understand the optimum number of layers required. As shown in Figure 4.17, 2 mg/L of Cd (II) ions aqueous solution, pH value of 7, 150 rpm mixing rate, 15 minutes contact time, 298 K temperature and 4g/L of the adsorbents prepared $(PEFA)_{n,}$ where n is 0. 1, 2 3, 4, 5…20 and is depicted as the number of layers were used for this study. When n is 0, this is regarded as no layer and it is known as AFA (acid-treated fly ash). Maximum removal was attained by at n = 5 with 96 % removal efficiency, followed by $(PEFA)_3$ and $(PEFA)_2$ with 92 and 89 % removal respectively. The optimum result obtained with $(PEFA)_5$ can be attributed to the presence of greater number of adsorption sites available for ion binding. As seen in Figure 4.17, the rate of Cd (II) ion sorption increases as n increases from 1-5, however, sorption rate decreases at n > 5. Also, steady increase was observed from 15-20 layers. This implies that as the number of layers increases, more binding sites become available for sorption, due to the increasing physiosorption phenomena being more predominant and ability of the Cd (II) ion to get into the pores as there is attraction between the FA surface and the Cd (II) ions in solution. In addition, there is availability of more active sites that aid Cd (II) ion sorption coupled with the fact that a non-coated fly ash (FA) adsorb ions via the physical mechanism by trapping ions in its pore spaces. Therefore, as inferred from the above explanations, we can infer that as there is increase PE layers on the FA, the mechanism of adsorption could likely be governed by physical sorption and ion exchange attraction rather than chemical sorption which may have influenced the rate of uptake of Cd (II) ions.

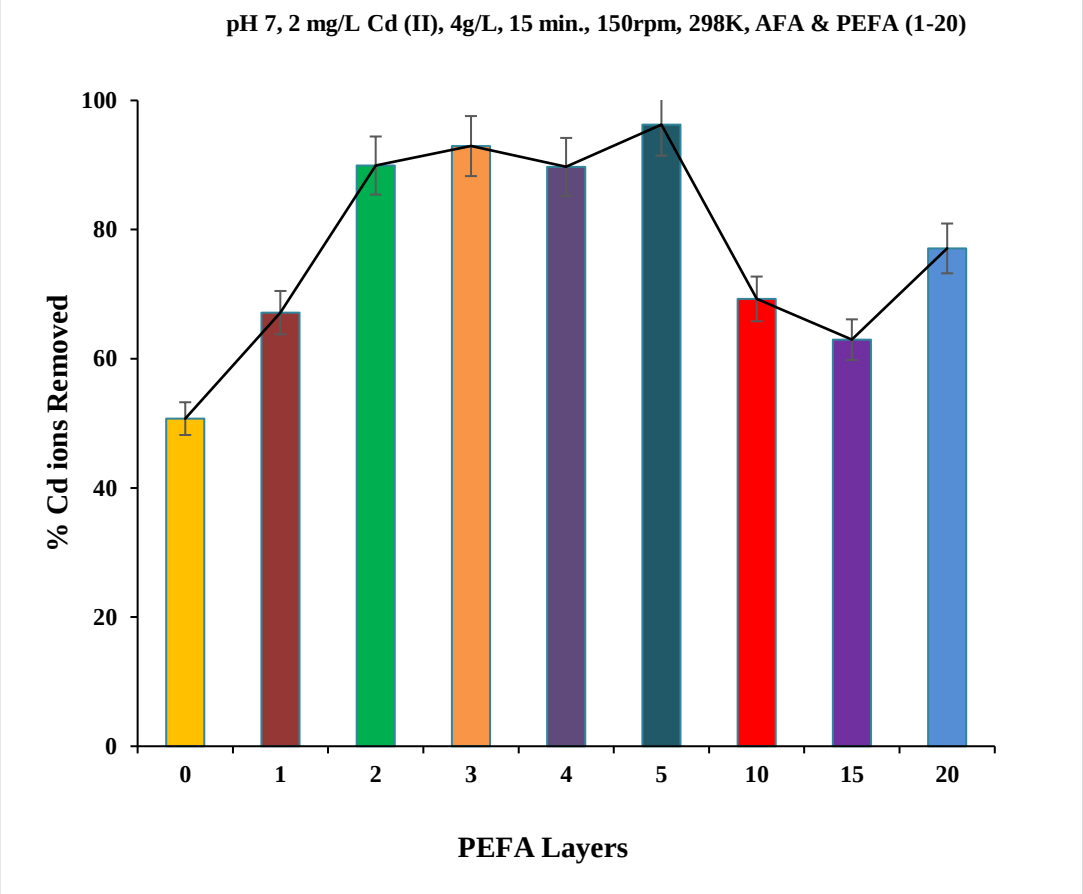

Figure 4.17 The effect of PEFA layers on the percent removal of Cd (II) ions on FA based adsorbents

4.3 Desorption Study

A potential adsorbent with good removal efficiency for metal ions must also have the ability to desorb the metal ions for recycling purposes (Akintola et al., 2016; Rathod et al., 2015; Akpomie et al., 2015). Based on the aforementioned fact, it was pertinent to study the desorption of Cd (II) ions from AFA, $(PEFA)_5$ and $(PEFA)_{20}$ surfaces. 0.1 M HNO_3 was used in desorbing the metal ions from the loaded adsorbents. The desorption efficiency of AFA was 61 % as compared to $(PEFA)_5$ and $(PEFA)_{20}$ with 55 and 35 % respectively as shown in Figure 4.18. This also suggests that both physiosorption and chemisorption might have been involved in the adsorption process (Meitei & Prasad, 2013; Abdel -Aty et al, 2013; S. Yang et al., 2013).

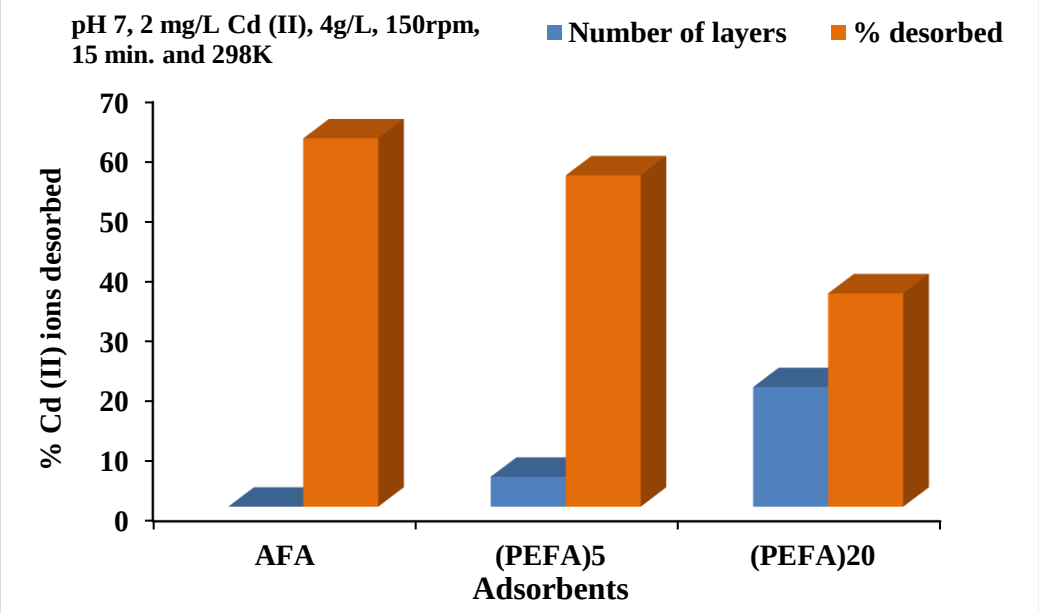

Figure 4.18 The percent desorption of Cd (II) ions on FA based adsorbents (AFA, $(PEFA)_5$ and $(PEFA)_{20}$) surfaces

4.4 Adsorption Isotherm Models

4.4.1 Langmuir and Freundlich Isotherm Models

Figure 4.19 and 4.20 illustrate Langmuir and Freundlich isotherm model for Cd (II) at pH (7). The maximum sorption capacity and adsorption intensity values were calculated from the slope and intercept of the plots between $1/q_e$ against $1/C_e$ for Langmuir as in q_m & K_L (Langmuir, 1918) and ln q_e against ln C_e for Freundlich as in K_f & n respectively (Freundlich, 1906). Table 4.3 indicates the values of correlation coefficient values (R^2) for both Langmuir and Freundlich as well as other parameters. This implies that both models fitted well for the experimental data. Nonetheless, the important features of Langmuir parameters can be applied to further forecast the interaction between the adsorbate and adsorbent with the aid of dimensionless separation parameters (R_L). R_L value gives essential information on sorption nature. R_L value for this study as shown in Table 4.3 indicate a favorable adsorption process ($R_L < 1$) for 2 mg/L Cd (II) ion concentration (Rathod et al., 2015; Kovo G. Akpomie et al., 2015; McKay et al., 1999). Adsorption of PEFA can also be explained in terms of surface area coverage in contrast to initial concentration of Cd ion (Rathod et al., 2015). Langmuir model for surface area coverage of adsorbent surface can be illustrated with aid of equation 4.5 below:

$$K_L C_i = \frac{\theta}{1-\theta} \qquad (4.5)$$

Where the surface area coverage of adsorbent surface is denoted as θ.

Table 4.3 Langmuir and Freundlich constants for Cd (II) ion uptake

	Langmuir constants					Freundlich constants		
	R^2	K_L	Q_{max}	R_L	Θ	R^2	K_f	n
20L	0.968	4.08	0.62	0.11	0.89	0.938	2.06	3.87
5L	0.931	18.12	0.89	0.03	0.97	0.952	1.15	4.36

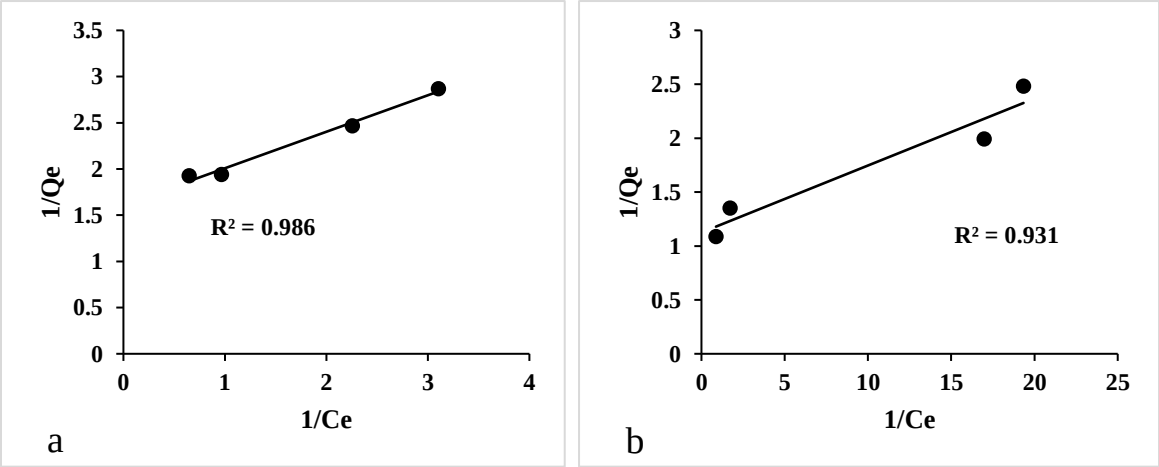

Figure 4.19 Langmuir adsorption isotherm models for (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

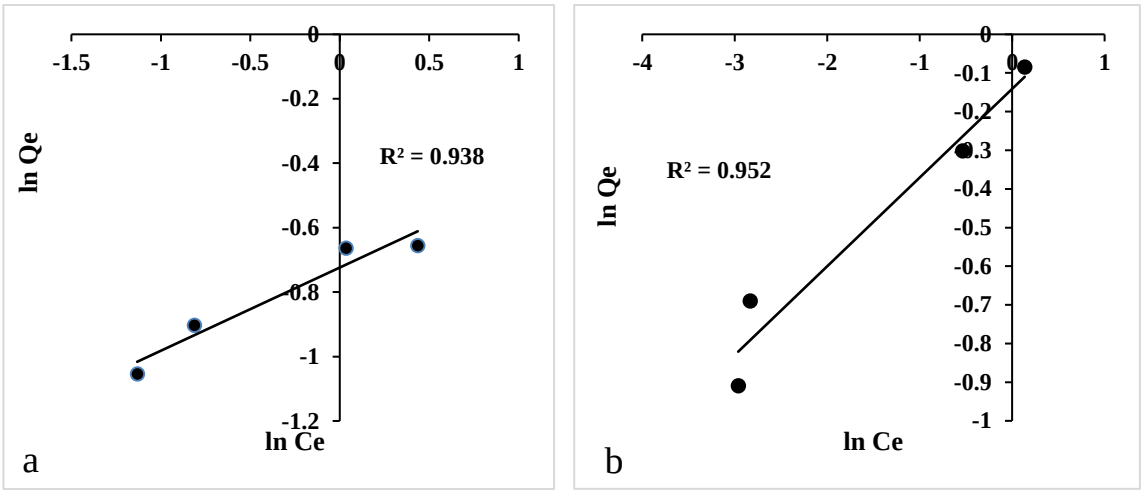

Figure 4.20 Freundlich adsorption isotherm models for (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

The R^2 values 0.931 and 0.986 obtained for $(PEFA)_5$ and $(PEFA)_{20}$ respectively shows the applicability of the Langmuir model for both adsorbents. The monolayer adsorption capacities of $(PEFA)_5$ and $(PEFA)_{20}$ are 0.89 and 0.62 mg/g respectively, the dimensionless separation values of both adsorbents were between 0 and 1, which point towards the fact that both has high affinity for Cd (II) ions.

The Freundlich R^2 values 0.952 and 0.938 obtained for $(PEFA)_5$ and $(PEFA)_{20}$ respectively gave good fit to the experimental data. In addition, the magnitude of n value can be used to identify the kind of mechanism involved. If the n value is less than or equal to 1, the process is chemisorption but if it is greater than 1, then the process is favors physiosorption mechanism. In this study, the n values recorded favors physical sorption between the adsorbents ($(PEFA)_5$ and $(PEFA)_{20}$) and Cd (II) ions.

4.4.2 Scatchard Plot Analysis

The Scatchard plot can be used to predict the kinds of interaction between the adsorbents and Cd (II) ions in aqueous solution (Scatchard, 1949). Though the adsorption parameters

are not applicable in a model like this but the nature of the plot can be likened to the kind of interaction of the chemical species on the adsorbents and metal ions (Gürten et al, 2005). A linear plot with negative slope indicates that interactions between metal ions and adsorbents binding sites follows Langmuir model. Also, the linear plot can be in form of a concave or convex shape. If it is convex (i.e. concave-up), with a slope less than 1, then negative cooperativity is detected, but if the linear plot is concave, the interaction is governed by a positive cooperativity phenomenon between strong and weak binding sites (Invitrogen Corporation, 2008). For this study, R^2 for both adsorbents ($(PEFA)_5$ and $(PEFA)_{20}$) as shown in Table 4.4 and Figure 4.21 shows conformity to linearity with negative slopes, this implies that the interaction between Cd (II) ions and adsorbents binding sites follows Langmuir model. Additionally, $(PEFA)_{20}$ has a concave curve which means that the interaction between the adsorbent surface and Cd (II) ions is governed by positive cooperativity between strong and weak binding sites. Meanwhile, $(PE\text{-}FA)_5$ was both concave and convex shows positive and negative cooperativity, which indicate the presences of two kind of binding sites.

Table 4.4 Scathard plot isotherm constants for Cd (II) ion uptake

		R^2	b	Q_s
Scathard plot	20L	0.965	-4.07	0.62
	5L	0.869	-16.48	0.91

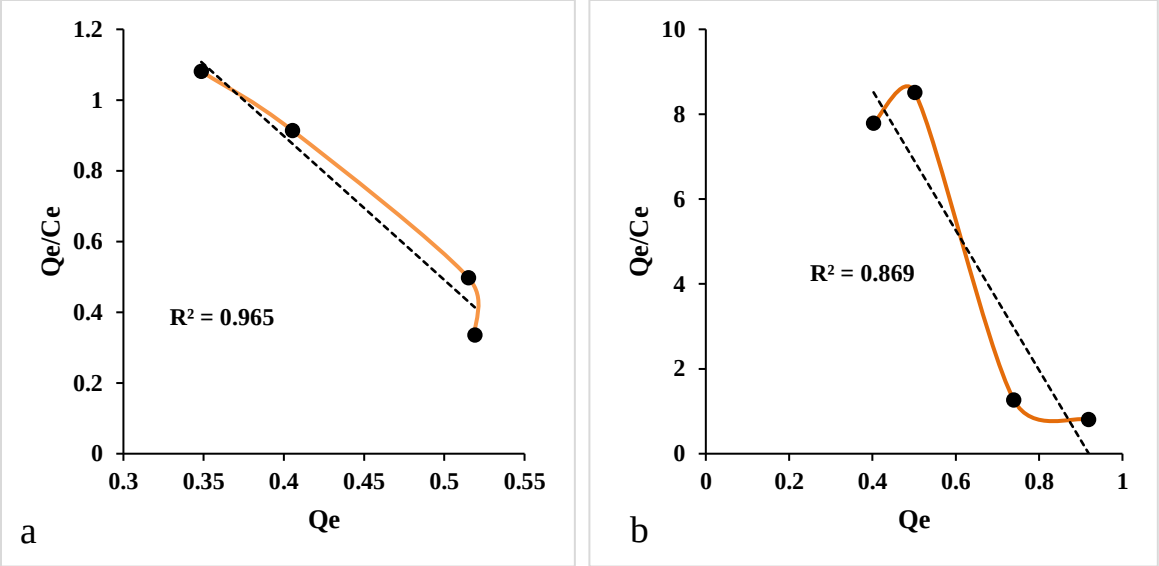

Figure 4.21 Scatchard plot analysis for (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

4.5 Kinetic Study for Adsorption

As indicated in equations 3.11, 3.12 and 3.13, kinetic studies of sorption data were evaluated by different kinetic models like pseudo 1st order, pseudo 2nd order and intra-particle diffusion (Leyva-Ramos et al., 1997; McKay et al., 1999; Weber, 1972). Sorption of cadmium ions were supervised at different period of time. Sorption Cd (II) ions was calculated from data acquired. To determine appropriate kinetic model, Cd (II) ion adsorption was plotted against time. These data were fitted into pseudo 1st order, pseudo 2nd order and Weber intra-particle diffusion equations (Leyva-Ramos et al., 1997). Table 4.5 indicate values of q_e and K_i were calculated from the K_i (Slope) and lnq_e (intercept) of plot $\ln(q_e - q_t)$ vs t in Figure 4.22. The correlation coefficient values (R^2= 0.971 and 0.909 for $(PEFA)_{20}$ and $(PEFA)_5$ respectively) for pseudo 1st order was lower than that of pseudo 2nd order as shown in Table 4.5. This could be link to the fact that sorption kinetics involves forces of valency via ions sharing or electron exchange between adsorbent and

the adsorbed ions on PEFA surfaces (Akpomie & Dawodu, 2015; Septhum et al, 2007). Values q_e and K_2 were calculated from q_e and $1/q_e$(slope) and $1/K_2 q_{e^2}$ (intercept) of the plot shown in Figure 4.23. The correlation (R^2= 0.999 and 0.999 for $(PEFA)_{20}$ and $(PEFA)_5$ respectively) for pseudo 2nd order were very stronger and it point toward the fact that sorption of Cd (II) ions occurs on a monolayer mode (Rathod et al., 2015). This means Cd (II) ions are bounded to definite active sites on the surface of for $(PEFA)_{20}$ and $(PEFA)_5$ respectively.

Weber and Morris intra-particle diffusion equation were also plotted for q_t against $t^{1/2}$ (Weber, 1972). Values of K_i and C were calculated from K_i(slope) and C (intercept) as display in Table 4.5 below. It correlation values (R^2= 0.975 and 0.812 $(PEFA)_{20}$ and $(PEFA)_5$ respectively) were the lowest and the plot intercept did not pass through the origin which point toward some control of boundary layers and suggest that intra-particle pore diffusion is not the only rate limiting factor (Rathod et al., 2015). The intra-particle diffusion equation plot indicates multilinearity notifying that three steps takes place. The initial sharper part is likened to the diffusion of Cd (II) ions via the solution to the external surfaces of PEFA or boundary layer diffusion of solid molecules (Han et al., 2006). The second part give description of ion phase where intra-particle diffusion is a rate limiting factor. The third part is ascribed to the final equilibrium phase. Nonetheless, the intercept of the plot fails to pass through the origin as seen in Figure 4.24. This may be attributed to the difference in the rate of mass transfer in the initial and final phase of sorption (Panday et al, 1986).

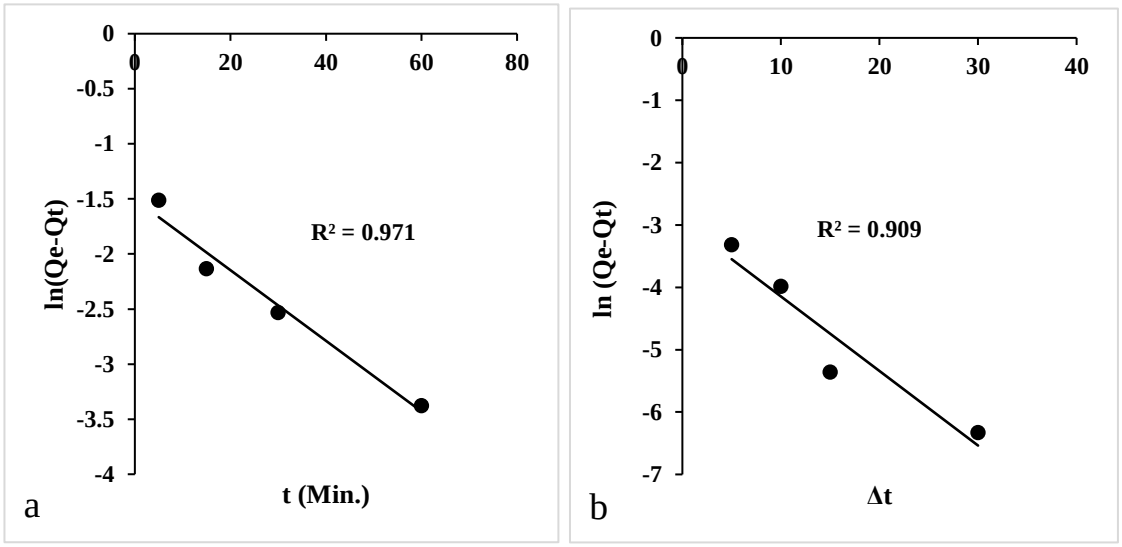

Figure 4.22 Pseudo 1st order model for (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

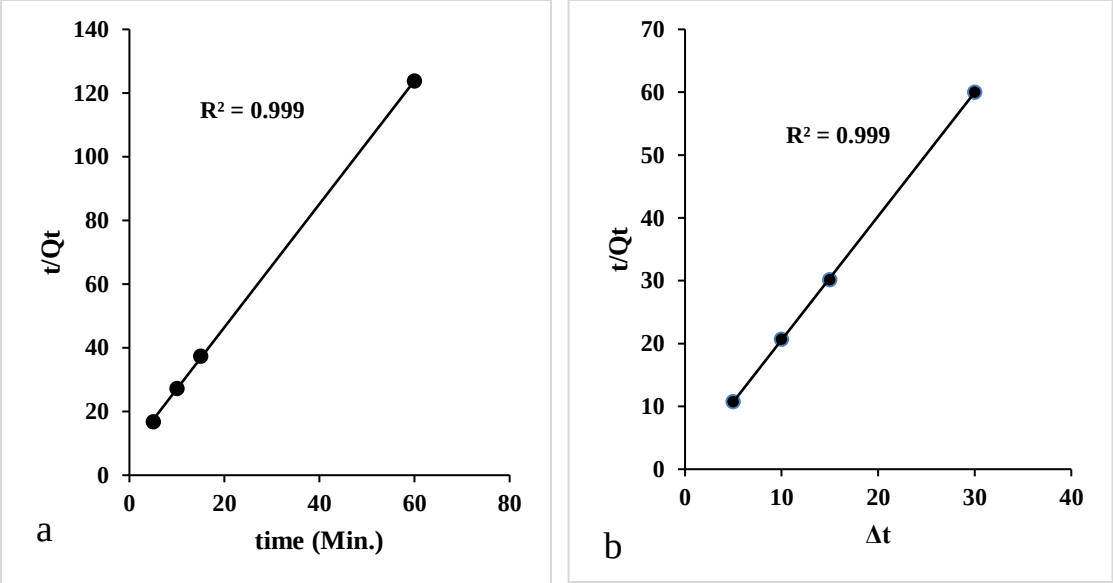

Figure 4.23 Pseudo 2nd order model for (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

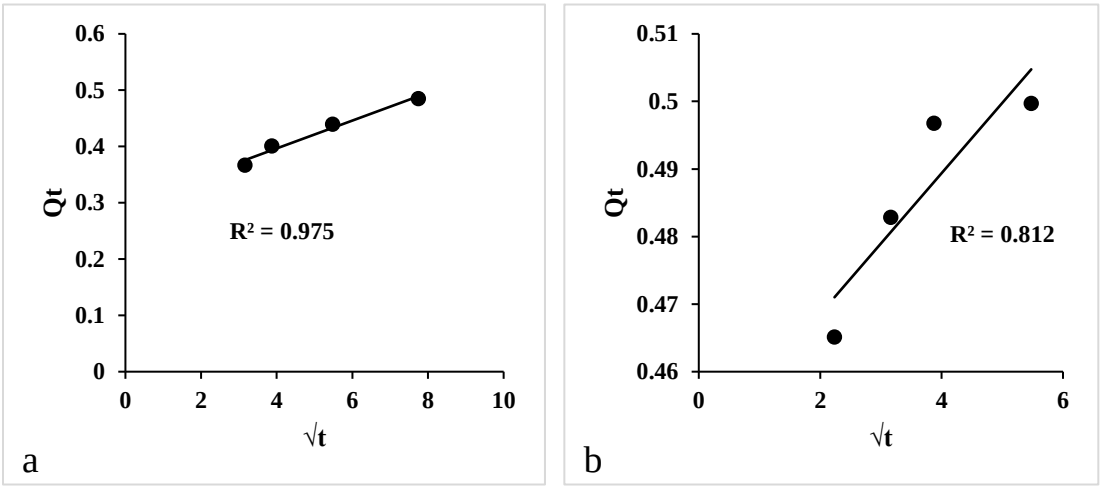

Figure 4.24 Weber-Morris intra-particle diffusion model for Cd (II) ion adsorption by (a) $(PEFA)_{20}$ (b) $(PEFA)_5$

Table 4.5 Sorption kinetics parameters for Cd (II) ion adsorption by PEFA

	Pseudo 1st order			**Pseudo 2nd order**			**Intra-particle diffusion**		
	Q_e	K_1	R^2	Q_e	K_2	R^2	K_i	C	R^2
20L	4.51	0.03	0.971	0.52	0.48	0.999	0.03	0.30	0.975
5L	19.13	0.12	0.909	0.51	4.44	0.999	0.01	0.45	0.812

4.6 Comparative Analysis of Adsorbents on Cd (II) ions Removal

The description of results obtained in this study was compared with similar research works. The removal efficiency of other works was compared to this work. Table 4.6 shows comparison between various adsorbents and their percent Cd (II) ions uptakes.

Table 4.6 Comparison of adsorbents on Cd (II) ions uptake

Adsorbent Types	**Conditions**				**Reference**
	pH	Initial Conc. (ppm)	Dosage (g/L)	Adsorption Capacity (Qe)	
Bagasse Fly Ash	6.0	14	10	1.18	Gupta et al (2003)
Barley Hull ash & Barley Hull	9.0	100	10	10.1	Maleki et al. (2011)
Acid modified Bagasse Fly Ash	5.0	50	1.6	25.1	(El-sherif & Fathy, 2013)
AC, CNT, CNF & FA	7.0	2	1	1.83	(Al-Khaldi et al., 2015)
Modified (AC, CNT, CNF & FA)	7.0	2	1	1.58	(Ihsanullah et al., 2015)
$(PEFA)_5$	9.0	2	4	0.89	This study

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This study demonstrated that the enhancement of FA surface charge with polyelectrolytes was successful in the removal of Cd (II) ion from aqueous solutions. The adsorption experiment study revealed that the binding of Cd (II) ions to PEFA surface was dependent on various factors such as pH of aqueous solution, adsorbent dose, contact time, mixing rate, Cd (II) ion initial concentration, temperature and number of PE coated layers.

The structural, elemental and thermal characterization of the PE coated adsorbent (PEFA) indicated a successful coated surface of FA. The adsorbent performed superior to RFA and AFA in the removal of Cd (II) ions from aqueous solution with excellent results in all varied conditions at shorter contact time. A removal of approximately 99 % of Cd (II) was achieved at pH 7, 15 min contact time, 2 mg/L Cd (II) ion initial concentration, 4 g/L dose of adsorbent, 150 rpm mixing rate, at 298 k and 5 layers of PE coated FA.

Langmuir isotherm model was found to fit well for $(PEFA)_{20}$ with R^2 value of 0.968 and Freundlich isotherm model to fit well for $(PEFA)_5$ with R^2 value of 0.952 implying that $(PEFA)_{20}$ adsorption of Cd (II) ions took place on homogeneous binding sites and $(PEFA)_5$ on heterogeneous binding sites. The adsorption kinetics aligned with pseudo second order model. The investigation of thermodynamic parameters also suggested that adsorption of

Cd (II) ions interaction with PEFA was endothermic, spontaneous and increasing disorderliness of solute solution interface. The study of number of PEFA layers suggested that the mechanism of adsorption of Cd (II) ions onto PEFA surface was governed by physical sorption and ion exchange attraction.

Finally, this research revealed that with FA as a hazardous waste requiring management, its application in water treatment for the removal of toxic heavy metals could be a potential way to make use of it.

5.2 Recommendations

It is recommended that further studies can be conducted to demonstrate the following research points:

1. The polyelectrolytes used in this study (PDADMAC-PSS) can be applied to modify other notable adsorbents such as carbon nanofibers (CNF), carbon nanotube (CNT) etc.
2. The adsorbent synthesized in this study (PEFA) can be tested for the removal of other pollutants such as Pb, Cr, Mn, and Cu.
3. The adsorbent synthesized in this study (PEFA) can be tested for the removal of multi pollutants.
4. The study of adsorbents dose (i.e. PEFA modified) should include particle size and its effect on heavy metals as well as their characterization.

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